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THE ASSOCIATION OF AUTOMOTIVE FUEL COMPOSITION WITH EXHAUST REACTIVITY

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The Association of Automotive Fuel Composition With Exhaust Reactivity

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CONTENTS

	Page
Abstract	1
Introduction	1
Experimental design and procedures	3
Selection of test fuels	3
Tests using gasolines	5
Smog chamber tests using gasolines	10
Testing of simple hydrocarbon fuels	10
Results--discussion	11
Tests using gasolines	11
Smog chamber program	21
Influence of engine air-fuel ratio (A/F) on correlation results	33
Automotive combustion of simple hydrocarbon fuels	37
Summary and conclusions	41
References	43
Appendix.--Analysis of exhaust mass emission data	45

ILLUSTRATIONS

1.	Correlation of calculated exhaust reactivities with polyalkylbenzene levels in fuel	18
2.	Correlation of calculated exhaust reactivities with olefin levels in fuel	19
3.	Correlation of observed exhaust reactivities with total aromatic levels in fuel	26
4.	Comparison of exhaust reactivities--fuel aromatic relationships from two Bureau of Mines studies	27
5.	Correlation of observed exhaust reactivities with polyalkylbenzene levels in fuel	28
6.	Correlation of observed and calculated (Jackson scale) exhaust R_{NO_2} reactivities	29
7.	Correlation of observed exhaust R_{NO_2} reactivities with calculated reactivities by Jackson and Bureau of Mines scales	32
8.	Correlation of observed exhaust reactivities with calculated "fuel" reactivities	34
9.	Calculated R_{NO_2} reactivities of exhaust from simple hydrocarbon fuels used under varied A/F conditions	35
10.	Calculated R_{NO_2} reactivities of exhaust from gasoline fuels used under varied air-fuel ratio conditions	36
11.	Correlation of observed and calculated R_{NO_2} reactivities of exhaust from simple hydrocarbon fuels	40
A-1.	Average emission levels for each car and each fuel	48
A-2.	Variation of exhaust mass emission parameters with various fuel composition parameters	50

TABLES

1.	Experimental fuels used in the gasoline fuel test program	6

TABLES--Continued

		Page
2.	Experimental fuels used in the simple hydrocarbon fuel testing program	9
3.	Test automobiles	9
4.	Mass emissions and molar specific reactivity of exhaust in first phase of fleet testing program	12
5.	Mass emissions and molar specific reactivity of exhaust in second phase of fleet testing program	14
6.	Correlation of exhaust composition with fuel composition for car No. 5	17
7.	Correlation of exhaust composition with fuel composition, car dummy variables, and air-fuel ratio	20
8.	Smog chamber reactivities of exhaust from fuels 1-21	22
9.	Smog chamber reactivities of exhaust from fuels 22-25	30
10.	Bureau of Mines rate-of-NO_2-formation reactivity scale	31
11.	Composition and smog chamber reactivities of exhaust from simple hydrocarbon fuels	38
12.	Summary of smog chamber reactivities of exhaust from simple fuels	39
A-1.	Summary of mass emission data for five cars and 10 fuels	46
A-2.	List of fuel physical and compositional properties used in correlations	46
A-3.	Correlation coefficients for exhaust mass emission levels and fuel physical and compositional properties	47
A-4.	Summary of regression analysis results	47

THE ASSOCIATION OF AUTOMOTIVE FUEL COMPOSITION WITH EXHAUST REACTIVITY

by

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ABSTRACT

The association of automotive fuel composition with exhaust reactivity was studied in an experimental program that involved testing with different automotive engines and with gasolines of varied composition. Results showed clearly the exhaust reactivity to increase with increasing levels of polyalkylbenzenes in the fuel. No other systematic patterns of high significance were detected in the association of exhaust reactivity with several broadly defined groups of fuel components. For the purposes of this study, had it been possible, fuel composition should have been defined and expressed in terms of component groups such that the potential for exhaust reactivity would be the same within each group and different from group to group. Classification of fuel components in terms of the paraffins-olefins-aromatics groups does not meet the latter requirements. For appropriate classification of fuel components more information is needed on the combustion of hydrocarbons in the multicylinder internal combustion engine. Statistical analysis of the mass emissions data showed significant car and fuel effects on hydrocarbon, carbon monoxide, nitric oxide, total aldehydes, and formaldehyde emission levels and on total photochemical reactivity. Car-fuel interactions were not significant at the 90-pct level. Correlations were found between mass emission parameters and fuel composition.

INTRODUCTION

Presently and undoubtedly for a large part of the decade of the 1970's, a major portion of efforts in air pollution abatement has been and will continue to be directed to reducing emissions from automobiles. Of the objectionable automotive emissions, the hydrocarbons are prominent because of their principal role in photochemical smog formation. As a result, several control methods for hydrocarbons have been devised, some of which have already been put to use while others are being further developed for use in the future. In most

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of these methods the approach is to use engine modification or accessory devices that would decrease the amount of hydrocarbon unburned in the primary combustion or convert the hydrocarbon emission into harmless product. This "device" or engine modification approach to emission control appears to have the potential for virtually complete elimination of the hydrocarbon emissions. A drawback, however, is the problem of retrofitting the automobiles already on the road.

Adjustment of fuel formula also could effect emission reduction either through reduction of emission levels or through emission modification resulting in less polluting material. While this "fuel optimization" approach may have only a modest potential for emission reduction per automobile, it has the advantage over the "device" approach that its application automatically encompasses all automobiles on the road.

The direction of the hydrocarbon control effort took a decisive turn with the recent setting of hydrocarbon emission standards for the 1975 automobiles (12).[5] The stringency of these standards almost eliminated for 1975 and 1976 model automobiles all control options except the ones in which catalytic exhaust conversion devices are used. Such devices as have been developed, however, do not function effectively with fuels containing lead antiknock additives because of the poisoning effect of lead on the catalyst. Therefore, an inevitable part of the control measure necessary to meet the 1975 automobile standards is the reformulation of gasoline to provide the requisite octane quality without the use of lead antiknock additives. The extent of reformulation required appears to have been lessened by a reduction in compression ratio that was put into effect to lower the octane requirement of the engines of 1971 and more recent automobiles. However, this engine modification has also affected engine efficiency adversely, and one should reasonably expect that in the years to come the tendency will be toward higher engine compression ratio and hence toward gasolines made of higher octane quality hydrocarbons.

Besides the octane-related change in fuel formula, additional fuel reformulation might become necessary as a result of new findings on the harmful effects of emissions. The present inventory of such effects is not necessarily complete. Chemical analysis of hydrocarbon combustion products, even though advanced methods were employed, has not yet yielded identification of each and every component of the complex mixture of exhaust emissions. For example, with the exception of the lead additive, virtually no information exists on the fate of fuel additives in the combustion process. Evidence of heretofore unknown objectionable exhaust components or effects arising from the use of additives might raise a need for new or revised control techniques including further fuel reformulation.

It would therefore appear that, based on present projection of control needs, modification of gasoline fuel composition is to be anticipated. While the principal objective of such modification is to alter the combustion

[5]Underlined numbers in parentheses refer to the list of references preceding the appendix.

characteristics of the basic fuel hydrocarbon mixture, it is also desirable that the fuel change be in the direction toward minimum pollution from emissions. Achievement of the latter would require reliable comprehensive information on the association of fuel composition with pollution potential of emissions in order to provide some guidelines for fuel reformulation.

Existing information on the association of fuel composition with pollution potential of emissions lacks needed detail and at points is conflicting. Earlier studies conducted in this Bureau of Mines laboratory (3, 11) suggested that fuel aromatics may be associated with organic emissions of higher photochemical smog potential or reactivity. Results from other studies (6, 15) suggested that such an effect of fuel aromatics is either small or none. All these previous studies of the fuel composition factor had the common inadequacy in that fuel composition was defined and expressed in terms of relative levels of broadly defined fuel component groups, namely, paraffins, olefins, and aromatics. These classifications disregard possible effects of differing composition within each of these groups. Lacking evidence to the contrary, one cannot neglect the possibility that such effects may be as strong or stronger than those effects associated with each of the parent groups.

This report covers work done at the Bartlesville Energy Research Center in cooperation with the Environmental Protection Agency to further explore the association of fuel composition with pollution character of emissions. In view of the importance of the current issue regarding the effect of fuel aromatics on emission reactivity, this research was designed, in part, to provide information directly relevant to this issue. Further, attempts were made to determine more precisely the fuel-emission association by expressing fuel composition in terms of fuel component groups more narrowly defined than in the previous studies.

EXPERIMENTAL DESIGN AND PROCEDURES

Selection of Test Fuels

Ideally, in a study of fuel composition effects, test fuels would be selected so that the level of each of the 200 or so fuel components varies from fuel to fuel independently of the levels of other components. For example, for 200 components and two levels per component, a factorial experiment would require that about 2^{200} test fuels be used to determine main and interaction effects of the 200 components. If these effects vary with each different automobile, then additional tests will be required to determine the specific effect on each automobile tested. These requirements are clearly impractical, and some simplification of the objectives must be made if the study is to entail a manageable effort.

Simplification can be accomplished by classifying the fuel components into a number of groups and by designing the study so as to determine the relative effects of these component groups--rather than of the 200 individual components. The success of such a simplification depends on whether the fuel component classification is consistent with the study's objective. Thus, if the objective is to relate fuel composition with pollution characteristics of

fuel, then fuel composition ideally should be expressed in terms of component groups such that pollution characteristics would differ from group to group but would be similar within each group. The use of any other grouping scheme will result in a rating of the component groups used, based on their contributions to emission pollution, but will not reveal the full potential for fuel composition to influence pollution potential.

Available evidence suggests that fuel aromatics contribute to exhaust hydrocarbons mainly via unburned fuel and contribute only to a minor extent via combustion reactions that result in aromatic addition-products (9). This suggests that the reactivity of those exhaust hydrocarbons that originate from the fuel aromatics is determined mainly by the intrinsic reactivities of the aromatic hydrocarbons in the fuel. These reactivities are known to differ widely in value (8), and in a manner that justifies classification of fuel aromatics into three groups, in the following order of reactivity: polyalkylbenzenes > monoalkylbenzenes > benzene.

Relative to the aromatic fuel components, in typical automotive engine combustion the fuel paraffins are more readily burned or fragmented--fuel olefins even more easily oxidized. Therefore, the contribution of fuel paraffins and olefins to exhaust organics consists mainly of combustion products rather than unburned fuel. Further, combustion products from fuel paraffins and olefins are distinctly different than those from aromatics in that they contain higher levels of reactive olefins and aldehydes and lower levels of unreactive acetylenes. Therefore, fuel paraffins, olefins, and presumably naphthenes also, should be differentiated from aromatics, as having distinctly different combustion and pollution characteristics.

For further classification of the fuel aliphatics, the supporting evidence is sketchy. Such evidence and reasonable speculation suggest (1) relative to straight-chain fuel hydrocarbons, branched paraffins and olefins are more likely to yield exhaust olefins substituted at the double bond and such olefins are generally much more reactive than the straight-chain ones; and (2) relative to branched olefins, branched paraffins yield higher levels of exhaust olefins (7). Finally, it is also likely that fuel aliphatics differ significantly in pollution characteristics even within each of the groups of branched paraffins, branched olefins, straight chain paraffins, and straight chain olefins, depending on molecular size and structure. While there is no experimental evidence directly applicable to this point, it has been shown that at least in pyrolysis of hydrocarbons, the composition of final products differs greatly with structure differing within the group of branched paraffins (14).

Thus the available information justifies classification of fuel components on the basis of their contribution to exhaust pollution characteristics in at least the following detail: Benzene, monoalkylbenzenes, polyalkylbenzenes, olefins, branched paraffins, and straight chain paraffins. Further breakdown or an entirely different classification scheme based on molecular structure may be shown to be more appropriate if and when more information is generated on degradation patterns in automotive combustion of hydrocarbons.

The preceding considerations led to the design of 10 test fuels (fuels 12 to 21, table 1) that contained varying levels of benzene, monoalkylbenzenes, polyalkylbenzenes, n-paraffins, isoparaffins, cycloparaffins, n-butane, and olefins. Fuels listed as 1 to 9 in table 1 were test fuels used in a separate study of commercial gasolines (91-97-RON) marketed for use with the 1971 model year automobiles. Data from that fuel-evaluation program were found to be relevant to the objectives of the fuel composition effect study; therefore, data from both studies were pooled.

Fuels 10 and 11 (table 1) were commercial unleaded premium gasolines with unusually high levels of aromatics. These two fuels were also included in order to provide additional data on the effect of fuel aromatics on emission reactivity. Fuels 22 to 25 (table 1) were those used in an earlier Bureau of Mines study (3, 11) in which fuel aromatics were shown to have a strong effect on emission reactivity; these fuels were reused in this study in order that additional information could be added to that from which previous conclusions were drawn.

In addition to gasolines (fuels 1-25), a few simple hydrocarbon fuels (table 2) were also used in experiments in the small two-cylinder engine. The purpose of this work, as discussed later, was to gain information on the degree to which pollution characteristics of the various specific fuel hydrocarbons vary.

Tests Using Gasolines

The gasolines were studied using 11 automobiles (table 3) selected to represent typical, high production, late models.

Engines of automobiles in the test program were adjusted according to manufacturer's specifications. In the first phase of this program automobiles 1 through 9 were used in tests with eight fuels (fuels 1, 4-10, table 1). Each automobile was operated at 85° F ambient temperature following a 22.9-minute engine duty cycle (Federal cycle for 1972 automobiles and more recent ones (13)). Limited testing was also conducted at 45° and 20° F ambient temperatures. Samples of exhaust in mixture with air were drawn throughout the engine test as prescribed in Federal test procedures for 1972 automobiles (13).

In the second phase of the program, automobiles 5, 6, 7, 9, and 10 were used to test fuels 12 through 21. Each automobile was operated at 75° F ambient temperature following the same engine cycle as in the first phase. Exhaust was sampled as prescribed in Federal test procedures for 1975 automobiles (12); that is, three samples were collected to provide sample of (1) exhaust in the cold start part of the cycle, (2) in the remaining stabilized part, and (3) in the hot start part, respectively. In both phases of this study, exhaust was analyzed for individual hydrocarbons (4), total hydrocarbon by flame ionization detection (FID), total aldehydes (10), formaldehyde (1), oxides of nitrogen (NO_x) by nondispersive infrared (NDIR), carbon monoxide (CO) by NDIR, and carbon dioxide (CO_2) by NDIR. The data from these tests were used to associate fuel composition with exhaust hydrocarbon composition (without reference to experimentally observed reactivity or smog potential).

TABLE 1. - Experimental fuels used in the gasoline fuel test program

Specifications	Fuel No.								
	1	2	3	4	5	6	7	8	9
Grade	Regular	Regular	Regular	Regular	Regular	Regular	Special	Special	Special
RVP	10.4	9.1	11.3	10.2	9.3	8.3	10.1	11.5	10.0
Specific gravity	.725	.747	.746	.747	.731	.725	.707	.755	.738
TEL, ml/gal	0	0	.35	.34	1.90	1.80	0	0	0
Research octane No.	[1] 91	[1] 91	[1] 94	[1] 91	[1] 94	[1] 94	92	97	95
Distillation, ° F:									
IBP	88	96	100	106	105	92	88	88	86
10 percent	122	134	136	126	125	128	122	110	118
50 percent	210	234	240	220	199	198	218	215	230
90 percent	304	340	376	309	324	308	300	308	308
End	374	404	418	435	415	392	382	378	366
GLC composition, mole-percent:									
Paraffin	67.7	60.5	69.1	58.8	64.2	67.0	81.0	48.2	56.8
Olefin	9.0	7.6	6.7	13.0	10.2	6.2	4.5	6.6	7.4
Aromatic	23.3	31.9	24.2	28.2	25.6	26.8	14.6	45.2	35.8
Monoalkylbenzenes	8.8	10.0	3.3	6.8	6.6	9.1	4.3	14.3	11.1
Polyalkylbenzenes	12.1	20.6	20.3	20.2	18.3	15.3	8.2	23.9	19.8
n-Paraffins	21.4	16.3	21.5	18.1	22.9	19.5	21.3	23.6	19.8
Isoparaffins	41.4	38.9	37.6	34.9	36.1	42.4	58.0	22.2	35.0
Cycloparaffins	4.8	5.3	10.0	5.8	5.1	5.1	1.6	2.4	1.9

	Fuel No.							
	10	11	12	13	14	15	16	17
Grade	Premium	Premium	Special	Special	Special	Special	Special	Special
RVP	12.8	10.1	8.4	7.7	7.9	7.7	7.5	8.7
Specific gravity	.755	.771	.731	.731	.731	.762	.712	.748
TEL, ml/gal	0	0	0	0	0	0	0	0
Research octane No.	[1] 100	[1] 100	92	92	93	95	94	89
Distillation, ° F:								
IBP	86	92	108	100	102	106	108	105
10 percent	120	140	136	138	134	146	136	135
50 percent	230	240	186	186	202	226	168	213
90 percent	326	318	284	254	292	282	246	324
End	364	378	380	382	378	350	288	392
GLC composition, mole-percent:								
Paraffin	50.6	45.9	57.7	56.6	59.0	44.7	71.4	43.5
Olefin	1.2	2.1	9.7	9.8	10.1	4.9	0	19.3
Aromatic	48.2	52.0	32.6	33.7	31.0	50.4	28.6	37.2
Monoalkylbenzenes	33.8	28.5	12.6	30.3	2.4	24.6	12.0	13.6
Polyalkylbenzenes	14.2	23.0	12.8	3.1	28.3	25.6	9.7	16.2
n-Paraffins	14.8	11.4	20.0	19.3	20.2	23.1	17.7	21.6
Isoparaffins	35.3	34.0	34.7	34.2	35.7	18.9	52.6	17.6
Cycloparaffins	.5	.5	3.0	3.0	3.1	2.7	1.2	4.2

See footnote at end of table.

TABLE 1. - Experimental fuels used in the gasoline fuel test program--Continued

Specifications	Fuel No.							
	18	19	20	21	22	23	24	25
Grade	Special	Special	Special	Special	Premium	Regular	Premium	Regular
RVP	7.7	8.1	14.0	8.2	10.0	9.9	11.0	10.1
Specific gravity	.745	.751	.723	.761	.728	.738	.769	.744
TEL, ml/gal	0	0	0	0	2.6	2.0	0	0
Research octane No.	96	90	91	93	100	95	102	98
Distillation, ° F:								
IBP	103	100	90	107	88	90	87	88
10 percent	140	136	112	138	117	120	117	115
50 percent	200	188	186	222	221	212	238	204
90 percent	267	288	294	291	308	332	315	313
End	294	370	382	376	381	377	370	369
GLC composition, mole-percent:								
Paraffin	51.5	62.1	59.0	43.2	61.4	62.3	39.9	48.5
Olefin	0	8.7	9.2	9.2	11.1	15.9	10.7	17.2
Aromatic	48.5	29.2	31.8	47.7	27.6	21.9	50.0	34.3
Monoalkylbenzenes	23.4	12.5	12.6	13.8	20.3	6.6	19.6	10.1
Polyalkylbenzenes	18.7	11.9	12.8	27.0	7.0	14.9	27.8	22.0
n-Paraffins	22.3	20.0	31.8	24.2	23.1	13.1	2.3	5.8
Isoparaffins	26.3	10.3	24.2	15.4	37.3	39.9	36.1	40.2
Cycloparaffins	2.9	31.9	3.1	3.6	1.0	9.3	.9	2.6

[1] Estimates of research octane number from fuel specified.
GLC--gas liquid chromatography.
IBP--initial boiling point.
RVP--Reid vapor pressure.
TEL--tetraethyl lead.

TABLE 2. - Experimental fuels used in the simple hydrocarbon fuel testing program

n-Butane
2,2,4-Trimethylpentane
2,3,4-Trimethylpentane
Methylcyclopentane
Butene-1
cis and trans Hexenes - 2 and 3
2,4,4-Trimethylpentene-1
2,4,4-Trimethylpentene-2
Benzene
Toluene
m-Xylene
sec-Butylbenzene
Hexene-1 + benzene
n-Heptane + benzene
n-Heptane + toluene
n-Heptane + m-xylene
n-Heptane + 2,4,4-trimethylpentene-2

TABLE 3. - Test automobiles

Vehicle No.	Make	Model	Year	Engine displacement, CID	Compression ratio
1	Chevrolet.	Impala....	1968	327	8.8
2	Pontiac...	Catalina..	1968	400	8.6
3	Rambler...	Ambassador	1969	290	9.0
4	Oldsmobile	Cutlass...	1969	350	10.3
5	Chevrolet.	Impala....	1970	350	9.0
6	Plymouth..	Fury.....	1970	318	8.8
7	Ford.....	Fairlane..	1970	351	9.5
8	Chevrolet.	Biscayne..	1971	350	8.5
9	Ford.....	Custom....	1971	351	9.0
10	Plymouth..	Fury I....	1971	383	8.7
11	...do.....	Valiant...	1969	225	8.4

CID--Cubic-inch displacement.
NOTE: Vehicles 1 through 4 were equipped to meet the California emission standards of 1968-69.
Vehicles 5 through 10 were equipped with evaporative control devices.

Note that while the two phases of the program had somewhat different specific objectives and experimental conditions, their respective data, being relevant to the issue of fuel-emission association, were pooled together. For such pooling, analytical data from the three exhaust samples per test in the second phase were combined mathematically to yield data comparable to those obtained in the first phase. Also, the difference in test temperature between

the two phases (85° F versus 75° F) was judged to have no significant effect on the fuel-emission association and was, therefore, ignored.

This experimental program that involved the 11 automobiles was expected to provide data suitable and adequate to establish the association of fuel composition with exhaust hydrocarbon composition, but not with exhaust hydrocarbon reactivity. The latter limitation was because the exhaust samples from this program contained relatively high levels of NO_x that prohibited experimental measurement of exhaust hydrocarbon reactivity in photochemical smog chambers (2). For such measurement to be feasible, the hydrocarbon/NO_x ratio in exhaust must be higher than 3:1 (ppmC:ppm) (2); such a condition can be realized only when the automotive engine operates under richer than normal air-fuel (A/F) conditions. Alternative methods for estimating exhaust hydrocarbon reactivity from exhaust hydrocarbon composition have been shown to be much less reliable than direct experimental measurement (3). This consideration led to designing a separate program to study the association of fuel composition with exhaust hydrocarbon reactivity.

Smog Chamber Tests Using Gasolines

In the smog chamber program the experimental fuels (fuels 1-25, table 1) were studied using an automobile that was operated fuel-rich in order to yield exhaust with high hydrocarbon-to-NO_x ratio as required for smog chamber examination. Exhaust samples in this program were analyzed as in fleet testing and were also examined in a smog chamber for photochemical reactivity. For reactivity measurement, exhaust at the initial levels of 6 ppmC hydrocarbon, 0.9 ppm NO, and 0.1 ppm NO_2 was irradiated in a smog chamber following procedures described in the literature (2).

Because the test automobile in the smog chamber program was operated fuel-rich, the question was raised whether this perturbation in an engine operation condition would invalidate the findings of the smog chamber program. To investigate this, additional testing was conducted in which one automobile and one small two-cylinder engine were operated under varied A/F conditions, using gasolines as well as the simple hydrocarbon fuels.

Testing of Simple Hydrocarbon Fuels

Results from the gasoline testing program described in the preceding sections indicated a need for information on the automotive combustion characteristics of specific hydrocarbon types. More specifically, such information was needed to serve the following purposes:

1. To demonstrate the degree to which reactivity of exhaust from various hydrocarbons varies with hydrocarbon structure.

2. To provide guidelines for classifying hydrocarbons into groups such that the potential for exhaust reactivity would be different from group to group but uniform within each group.

The experimental program that was run was undertaken and designed with the first purpose in mind; to serve the second purpose, a much larger research effort would be necessary.

Fourteen prominent fuel compounds (table 2) were chosen to represent several classes of hydrocarbons in gasoline fuels. The fuels were run in a two-cylinder water-cooled engine (Onan) at three A/F equivalence ratios--0.75, 1.0, 1.1. For all tests, the engine was operated at 1,800 rpm (1,800 rated speed) and at one-fifth full load. Exhaust was sampled and analyzed for individual hydrocarbons by gas liquid chromatography (GLC), total hydrocarbon, formaldehyde, total aldehydes, NO_x, CO, and CO_2. Exhaust samples from the rich operation mode were also irradiated in the smog chamber for measurement of the photochemical reactivity. Duplicated chamber runs were conducted with initial exhaust level at 6.0 ppmC hydrocarbon, 0.9 ppm NO, and 0.1 ppm NO_2.

RESULTS--DISCUSSION

Tests Using Gasolines

Results from tests with the 11 automobiles are given in tables 4 and 5. The tabulated data are for emission rates of exhaust hydrocarbon, CO, NO_x, total aldehydes, and for hydrocarbon reactivities calculated from hydrocarbon compositions.

These results were analyzed statistically for correlations between fuel composition and exhaust emissions. Such correlations, if present, were to be interpreted to provide a measure of the relative contributions of fuel hydrocarbons to exhaust emissions. Correlations with exhaust emission rates are described and discussed in appendix A. The remainder of this section deals with the correlation of fuel composition with concentrations of reactive organics (hydrocarbons and aldehydes) in exhaust.

The exhaust parameters used in this correlation analysis included calculated reactivities, formaldehyde, total aldehydes, and several olefins and aromatics that are known to contribute significantly to exhaust reactivity. Varied schemes and combinations of hydrocarbon class and subclass division and groupings were used as parameters of fuel composition. Thus, in one attempt exhaust composition was correlated with fuel composition expressed in terms of paraffin, olefin, and aromatic. In other correlation models, fuel composition was expressed in terms of more narrowly defined component groups. Correlation analysis was applied upon data from each automobile separately. Using such data, the fuel-exhaust correlations were not obscured by car effects or car-fuel interaction effects. Such effects, while undesirable in the correlation analysis, are nevertheless of interest, and were explored in a separate statistical analysis.

TABLE 4. - Mass emissions and molar specific reactivity of exhaust in first phase of fleet testing program

(Each value is average of three tests)

Vehicle No.	Fuel No. 1	4	5	6	7	8	9	10	Mean	Standard deviation[1]	Coefficient of variation
HYDROCARBON, g/MILE											
1	4.02	4.16	4.15	4.05	4.04	3.98	3.86	3.84	4.02	0.20	5.0
2	3.91	3.71	4.09	3.89	3.90	3.51	3.36	3.96	3.79	.17	4.6
3	3.77	3.96	3.68	3.61	3.76	3.81	3.73	4.14	3.81	.19	5.1
4	2.84	2.88	3.03	2.99	2.91	3.38	3.04	3.24	3.04	.22	7.1
5	2.53	2.55	2.38	2.41	2.40	2.59	2.54	2.42	2.48	.29	11.6
6	5.70	4.48	4.82	4.57	5.12	5.23	5.22	8.09	5.40	.36	6.7
7	3.52	3.20	3.42	3.61	3.43	3.29	3.46	3.54	3.43	.17	4.9
8	2.51	2.36	2.62	2.21	2.46	2.40	2.10	3.17	2.48	.20	7.9
9	3.13	3.43	3.85	3.83	3.58	3.94	3.37	3.81	3.62	.20	5.5
Mean	3.55	3.41	3.56	3.45	3.51	3.57	3.41	4.02	-	-	-
Standard deviation[1]	.26	.23	.24	.19	.21	.21	.26	.29	-	-	-
Coefficient of variation	7.3	6.7	6.7	5.5	6.0	5.9	7.6	7.2	-	-	-
CARBON MONOXIDE, g/MILE											
1	37	34	32	32	29	26	25	30	30.8	4.0	13.0
2	38	32	34	32	29	27	21	34	30.7	2.8	9.2
3	40	39	35	36	34	40	34	42	37.6	4.4	11.6
4	48	47	44	54	53	56	43	57	50.2	4.7	9.3
5	42	35	28	32	38	48	45	36	38.0	8.0	21.0
6	71	55	54	48	59	70	62	106	65.7	5.3	8.0
7	34	29	32	33	34	34	33	38	33.2	3.2	9.8
8	30	28	26	24	34	35	28	53	32.4	3.6	11.2
9	30	35	34	33	37	49	34	47	37.4	3.8	10.3
Mean	41.2	37.0	35.5	36.2	38.5	42.8	36.2	49.7	-	-	-
Standard deviation[1]	4.3	3.0	4.5	4.0	4.2	6.3	6.5	5.0	-	-	-
Coefficient of variation	10.4	8.1	12.6	11.0	10.8	14.6	17.8	10.0	-	-	-

NITRIC OXIDE, AS NO_2, g/MILE											
1	6.7	8.2	6.7	7.3	7.9	6.5	8.4	7.4	7.4	0.7	9.8
2	10.0	10.8	11.5	10.1	13.0	8.6	9.8	11.4	10.7	1.1	10.1
3	5.6	5.8	5.9	6.2	7.1	5.5	6.5	5.8	6.1	.5	7.9
4	5.0	5.7	5.4	4.9	4.6	4.3	5.5	5.6	5.1	.3	5.1
5	2.6	3.0	2.7	2.6	2.2	2.6	2.5	2.6	2.6	.2	8.9
6	5.1	5.5	5.6	5.8	5.0	5.5	5.2	4.5	5.3	.3	5.4
7	3.7	3.7	3.6	3.3	3.1	3.9	3.4	3.6	3.5	.3	7.9
8	3.6	3.5	3.4	3.3	3.3	3.7	3.5	3.7	3.5	.2	6.1
9	4.1	4.9	5.3	5.2	4.0	4.9	4.6	4.5	4.7	.5	10.7
Mean	5.2	5.7	5.6	5.3	5.6	5.1	5.5	5.5	-	-	-
Standard deviation[1]	.5	.5	.5	.6	.7	.7	.5	.4	-	-	-
Coefficient of variation	9.1	8.5	9.3	11.0	11.8	13.0	9.0	7.3	-	-	-
TOTAL ALDEHYDES, g/MILE											
1	0.18	0.18	0.16	0.14	0.18	0.21	0.18	0.15	0.17	0.02	8.9
2	.22	.22	.22	.21	.25	.27	.22	.20	.23	.02	7.0
3	.16	.15	.15	.15	.15	.22	.14	.14	.16	.02	10.3
4	.15	.16	.15	.14	.16	.19	.16	.15	.16	.01	7.9
5	.11	.12	.14	.12	.13	.10	.12	.11	.12	.01	12.4
6	.19	.18	.16	.18	.20	.15	.19	.15	.17	.02	10.4
7	.18	.20	.16	.20	.23	.16	.19	.18	.19	.02	11.8
8	.19	.16	.17	.14	.20	.14	.18	.13	.16	.02	10.6
9	.21	.24	.25	.25	.22	.18	.21	.16	.21	.03	16.1
Mean	.18	.18	.17	.17	.20	.18	.18	.15	-	-	-
Standard deviation[1]	.01	.02	.03	.02	.03	.02	.02	.02	-	-	-
Coefficient of variation	5.6	11.1	17.6	11.8	15.0	11.1	11.1	13.3	-	-	-
EXHAUST HYDROCARBON REACTIVITIES, ETHYLENE EQUIVALENT, g/MILE											
1	2.16	2.30	2.31	2.11	2.17	1.80	2.05	1.65	2.09	0.09	4.1
2	2.17	2.12	2.38	2.09	1.98	1.63	2.03	1.77	2.02	.09	4.7
3	2.02	2.13	2.06	1.85	2.03	1.81	1.91	1.74	1.94	.09	4.7
4	1.59	1.65	1.72	1.54	1.77	1.40	1.40	1.42	1.56	.10	6.6
5	1.39	1.41	1.37	1.30	1.29	1.18	1.31	1.08	1.29	.14	10.7
6	2.94	2.47	2.73	2.41	2.58	2.42	2.51	3.17	2.65	.11	4.1
7	1.94	1.83	2.03	1.99	1.84	1.62	1.75	1.60	1.83	.08	4.5
8	1.44	1.46	1.57	1.25	1.46	1.16	1.09	1.47	1.36	.11	8.3
9	1.81	1.91	2.28	2.13	2.02	1.90	1.79	1.72	1.95	.12	6.0
Mean	1.76	1.93	2.05	1.84	1.90	1.66	1.76	1.73	-	-	-
Standard deviation[1]	.09	.13	.12	.10	.10	.09	.13	.09	-	-	-
Coefficient of variation	4.3	6.2	5.8	5.4	5.1	5.4	7.6	5.1	-	-	-

[1]Standard deviation calculated from the three replicates on each car fuel combination.

TABLE 5. - Mass emissions and molar specific reactivity of exhaust in second phase of fleet testing program

(Each value is an average of three tests, time weighted, according to the cold start transient and stabilized portions of the Federal test procedure for 1975 automobiles)

Vehicle No.	Fuel No.										Mean	Standard deviation[1]	Coefficient of variation
	12	13	14	15	16	17	18	19	20	21			
EXHAUST HYDROCARBON, g/MILE													
5	3.56	3.48	3.84	3.74	3.72	3.54	3.66	3.61	3.45	3.48	3.61	0.21	5.7
6	4.41	5.10	4.74	4.86	5.02	4.10	4.89	4.61	4.18	4.22	4.61	.30	6.6
7	3.07	3.26	3.07	3.37	3.75	2.83	3.54	3.03	2.97	3.24	3.21	.20	6.1
9	2.87	2.67	2.88	3.00	3.12	2.78	3.08	2.72	2.73	2.96	2.88	.17	5.9
10	3.16	3.30	3.28	3.20	3.37	2.88	3.43	2.99	3.08	3.00	3.17	.18	5.6
Mean	3.41	3.55	3.56	3.63	3.80	3.23	3.72	3.39	3.28	3.38	-	-	-
Standard deviation[1]	.29	.29	.33	.21	.14	.20	.23	.13	.18	.07	-	-	-
Coefficient of variation	8.4	8.0	9.3	5.9	3.7	6.1	6.2	3.8	5.4	2.0	-	-	-
EXHAUST CARBON MONOXIDE, g/MILE													
5	71	71	72	70	66	65	65	74	62	62	67.9	5.1	7.5
6	43	46	46	46	44	44	46	48	44	45	45.3	2.4	5.2
7	40	43	40	44	44	38	43	44	40	44	42.0	2.9	6.9
9	39	35	38	36	41	36	42	40	40	40	38.7	3.4	8.8
10	42	45	42	41	42	39	46	44	47	42	43.1	2.9	6.8
Mean	47.1	48.2	47.4	48.5	48.8	44.4	48.4	-	-	-	-	-	-
Standard deviation[1]	3.4	-	4.2	3.4	2.0	3.5	-	-	4.4	1.2	-	-	-
Coefficient of variation	7.3	10.2	8.9	7.2	4.1	7.8	7.3	6.5	9.4	2.7	-	-	-
EXHAUST NITRIC OXIDE, AS NO_2, g/MILE													
5	4.5	4.1	4.2	4.9	4.1	5.0	4.8	4.6	4.6	4.9	4.6	0.3	5.7
6	6.9	6.8	6.5	7.2	6.8	7.3	7.0	7.2	6.8	7.2	7.0	.1	1.7
7	5.0	4.7	4.7	5.6	5.0	5.3	5.5	5.1	5.3	5.6	5.2	.3	5.4
9	6.1	6.1	6.1	6.7	5.8	6.9	6.2	6.1	6.0	6.6	6.3	.3	4.8
10	6.1	5.8	5.7	6.5	5.5	6.7	6.1	6.3	5.7	6.6	6.1	.2	3.4
Mean	5.7	5.5	5.4	6.2	5.4	6.3	5.9	5.9	5.7	6.2	-	-	-
Standard deviation[1]	.2	.3	.1	.3	.2	.3	.3	.3	.1	.3	-	-	-
Coefficient of variation	3.3	6.0	2.6	4.0	4.3	4.1	5.5	4.5	1.6	4.7	-	-	-

EXHAUST TOTAL ALDEHYDES, g/MILE													
5	0.11	0.11	0.10	0.10	0.13	0.12	0.13	0.11	0.13	0.09	0.11	0.01	13.3
6	.18	.17	.19	.16	.17	.17	.16	.17	.17	.15	.17	.02	8.9
7	.16	.14	.14	.15	.19	.14	.15	.13	.15	.15	.15	.01	8.9
9	.18	.18	.17	.17	.19	.17	.16	.16	.17	.15	.17	.01	8.7
10	.16	.15	.17	.14	.17	.16	.14	.14	.15	.14	.15	.01	9.8
Mean	.16	.15	.15	.14	.17	.15	.15	.14	.15	.14	.15	-	-
Standard deviation[1]	.01	.02	.01	.01	.02	.02	.02	.01	.02	.01	-	-	-
Coefficient of variation	8.7	10.1	9.4	9.1	9.4	10.0	11.0	9.2	11.7	9.5	-	-	-
JACKSON MOLAR SPECIFIC REACTIVITY, ETHYLENE EQUIVALENTS[2]													
5	0.87	0.86	0.97	0.86	0.87	0.95	0.83	0.87	0.90	0.91	0.89	0.03	3.5
6	.96	.92	1.03	.90	.93	1.00	.83	.91	.95	.96	.94	.03	2.7
7	.95	.89	1.03	.86	.85	.99	.85	.91	.91	.90	.91	.03	3.7
9	1.02	1.04	1.11	1.00	.94	1.06	.90	.94	1.02	.96	1.00	.03	3.0
10	.95	.92	1.05	.94	.93	1.00	.86	.93	.91	.97	.95	.03	3.5
Mean	.95	.92	1.04	.92	.90	1.00	.86	.91	.94	.94	-	-	-
Standard deviation[1]	.04	.02	.02	.02	.03	.03	.04	.04	.02	.02	-	-	-
Coefficient of variation	4.2	2.6	2.3	2.6	3.2	3.4	4.6	4.2	2.1	2.6	-	-	-

[1]Standard deviation calculated from the three replicates on each car fuel combination.
[2]Molar reactivity of ethylene = 1.

The correlation models that were used and results from the correlation analysis are illustrated[6] by information summarized in table 6 for car 5. Degree of correlation is represented by the value of R_{SQ} in table 6, a high R_{SQ} value representing a high degree of correlation. From the data of table 6, apparently better fuel-exhaust correlations are generally obtained when fuel composition is expressed in terms of a more detailed classification of the fuel components. For example, breaking the aromatic portion of the fuel into benzene, monoalkylbenzenes, and polyalkylbenzenes (model II) gave a fuel-exhaust correlation that was improved over that obtained when the total of aromatics is used as one fuel component (model I). This suggests that the source of a reactive exhaust organic is associated with a narrowly defined group or even an individual fuel component rather than with a broadly defined class of fuel hydrocarbons. This is more clearly illustrated by the correlation results for exhaust toluene and xylenes (see table 6). Levels of toluene and xylenes in exhaust were found to correlate much better with fuel composition when fuel aromatics were broken into benzene, monoalkylbenzenes (mostly toluene) and polyalkylbenzenes (mostly xylenes), with R_{SQ} values increasing from 0.66 and 0.41 to 0.94 and 0.80, respectively, for car 5. Evidently this was so because exhaust toluene and xylenes originate almost entirely from the toluene and xylenes (in fuel) and not from all fuel aromatics. In line with this reasoning, the rather poor correlations of exhaust olefins with fuel composition might be due to inappropriate grouping of fuel components. If so, then better correlation could be obtained if fuel components were classified into groups such that yield in exhaust olefins would be uniform within each group. The rather narrow ranges in yields are another difficulty in the correlations for exhaust olefins as indicated by the standard deviations about the means as seen in table 6. For example, the standard deviation for ethylene is about 20 pct of the mean value as compared with about 60 pct for toluene. Also, for low-yield components such as 2-methyl-butene-2, the experimental error in the concentration measurement may be important.

The main conclusion reached in consideration of the statistical data thus far is that better correlations of fuel composition with exhaust composition and calculated reactivity are obtained when fuel composition is expressed in more detail than is provided by the simple classification into paraffins, olefins, and aromatics. This statistical conclusion is interpreted to mean that pollution characteristics of fuel components vary considerably within the class of aromatics, as predicted by theory, and possibly within the paraffin and olefin classes also. Further interpretation of these statistical results--that is, to identify or quantitatively associate the source of an exhaust hydrocarbon with a specific group of fuel components--is not valid. Qualitative associations, however, might have significance. Thus, we examined the associations between calculated (Jackson) exhaust reactivity and the levels, in fuel, of aromatics, polyalkylbenzenes, olefins, paraffins, and isoparaffins. Systematic patterns were obtained only in the reactivity-versus-fuel

[6]Correlations were obtained from statistical analysis of data from each car examined individually. Results were similar, car-to-car, and the following discussion is to be construed as representing the typical case.

polyalkylbenzenes and reactivity-versus-fuel olefin plots (figs. 1 and 2), and even then the dependencies implied, although real, were nevertheless weak. Such failure to uncover strong dependence of exhaust reactivity on a specific group of fuel components may have been caused by the fact that the fuel component groups that were considered were inappropriately defined.

TABLE 6. - Correlation of exhaust composition with fuel composition for car No. 5

Exhaust composition parameter (Y)	Mean ($\bar{Y}$)	Standard deviation (S_y)	R_{SQ}[1]			
			Model I[2]	Model II[2]	Model III[2]	Model IV[2]
Ethylene	0.187	0.032	0.50	0.52	0.52	0.53
Propylene	.0728	.0116	.68	.69	.69	.69
iso + 1-Butenes	.0177	.0076	.46	.46	.47	.47
2-Methyl-2-butene	.0047	.0019	.002	.073	.007	.008
Toluene	.0596	.0359	.66	.94	.66	.95
m + p-Xylenes	.0324	.0194	.41	.80	.48	.84
$R_{Jackson}$	.8610	.0554	.44	.57	.45	.57
R_{EPA}	2.467	.122	.12	.55	.15	.55
Formaldehyde	.0347	.0099	.11	.17	.19	.21
Total aldehydes	.0595	.0147	.13	.16	.15	.17
Total ppm hydrocarbon	88.8	15.5	.02	.09	.07	.11
Total reactive grams (ethylene equivalents)	11.61	2.25	.15	.18	.21	.21

[1] R_{SQ} = The square of the multiple correlation coefficient.

[2] Model I: $Y = a_1$ (mole fraction [MF] paraffins) + a_2 (MF olefins) + a_3 (MF aromatics),

Model II: $Y = a_1$ (paraffins) + a_2 (olefins) + a_3 (benzene) + a_4 (monoalkylbenzenes) + a_5 (polyalkylbenzenes),

Model III: $Y = a_1$ (n-paraffins) + a_2 (isoparaffins) + a_3 (olefins) + a_4 (aromatics),

Model IV: $Y = a_1$ (n-paraffins) + a_2 (isoparaffins) + a_3 (olefins) + a_4 (benzene) + a_5 (monoalkylbenzenes) + a_6 (polyalkylbenzenes).

Since the analysis discussed thus far involved data from one automobile only, the question was raised whether the conclusions reached are valid for other automobiles also. It was also questioned whether whatever car effect exists is caused solely by air-fuel variation from car to car. To answer these questions, a statistical analysis was applied upon the data obtained in the second phase of the fleet testing program when A/F data were taken for all test cars. The statistical method used was similar to the one used in the fuel-exhaust correlation. Specifically, exhaust composition and calculated reactivity were again correlated with the fuel composition, except that this time, data from five automobiles were pooled and the correlation models used were as follows:

1. $(\text{Exh. component})_i = F$ (fuel composition),

2. $(\text{Exh. component})_i = F$ (fuel composition) + $a_1 c_1 + a_2 c_2 + a_3 c_3 + a_4 c_4$,

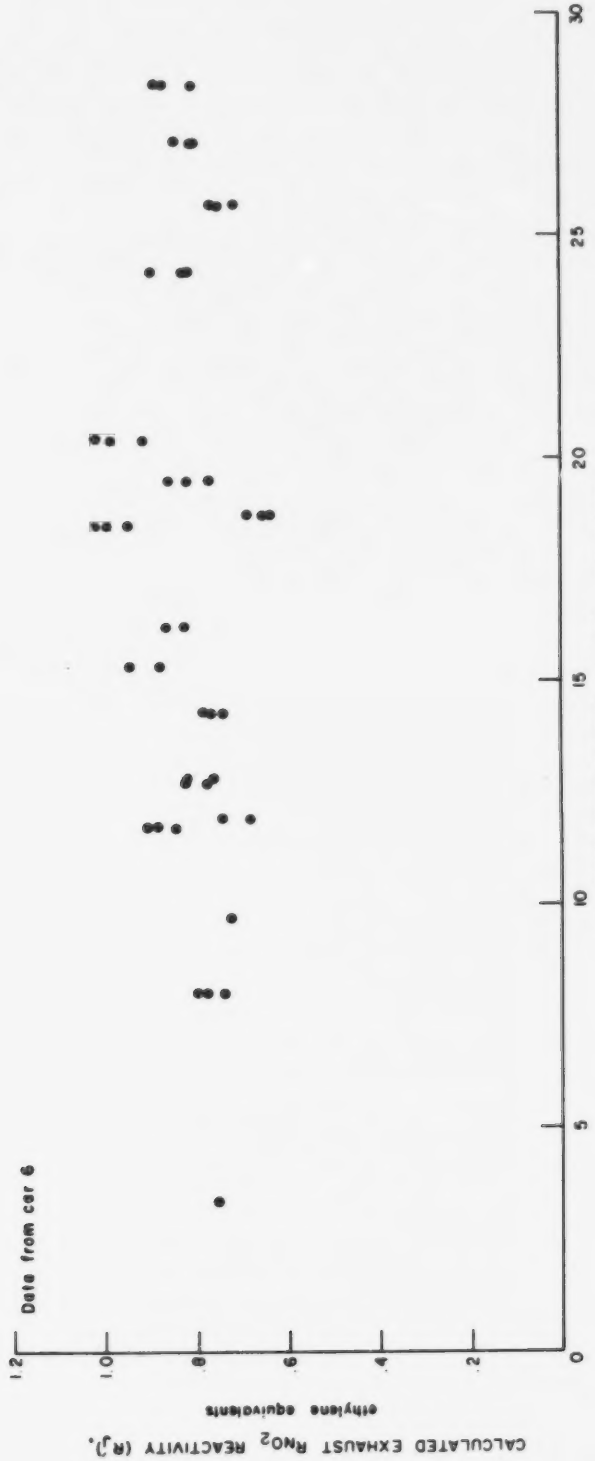

FIGURE 1. - Correlation of calculated exhaust reactivities with polyalkylbenzene levels in fuel.

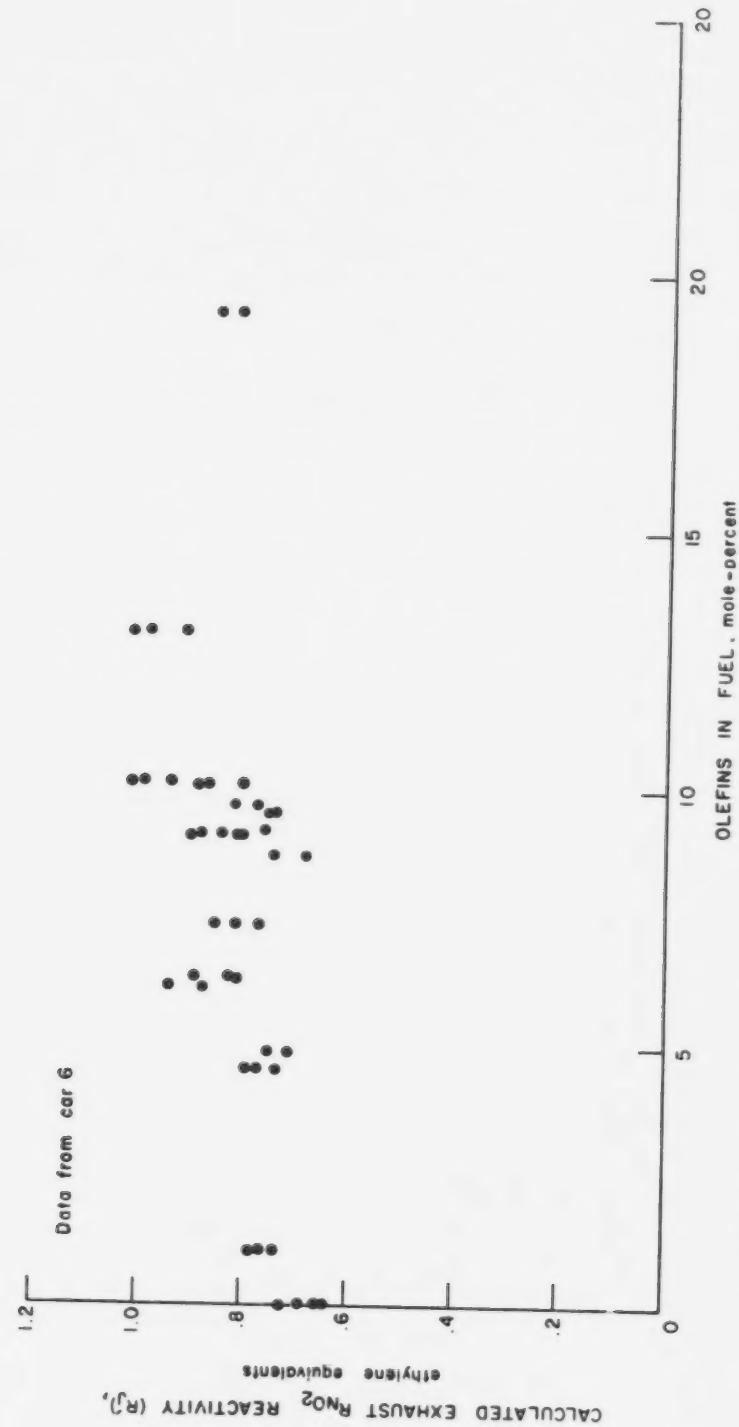

FIGURE 2. - Correlation of calculated exhaust reactivities with olefin levels in fuel.

3. (Exh. component)$_i$ = F (fuel composition) + a_1 (A/F).

Symbols are explained as follows:

F (fuel composition): function of fuel composition,

a_1c_1, a_2c_2, a_3c_3, a_4c_4: terms representing contributions of cars 6, 7, 9, and 10, to component i in the exhaust relative to that from car 5,

a_1 (A/F): term representing "contribution" of A/F to exhaust component i.

The experimental data were fitted to these statistical models and results were used to determine whether inclusion of the car or A/F variables improved the fuel-exhaust correlation. Results, summarized in table 7, show that inclusion of the car variables improved correlation substantially, suggesting, thus, presence of a strong car effect. Use of the A/F variable in lieu of the car variables had a much smaller effect, suggesting, thus, that the car effect was not a result of variation in average-over-the-engine-test A/F.

TABLE 7. - Correlation of exhaust composition with fuel composition, car dummy variables, and air-fuel ratio

(Data from second phase of fleet testing program)

Exhaust composition parameter	R_{sq}[1]		
	Model I[2]	Model II[2]	Model III[2]
Ethylene	0.41	0.85	0.45
Propylene	.28	.59	.40
iso + 1-Butenes	.35	.71	.46
2-Methyl-2-butene	.19	.33	.31
Toluene	.44	.47	.44
m + p-Xylenes	.42	.44	.42
$R_{Jackson}$	.26	.72	.35
R_{EPA}	.16	.71	.24
Formaldehyle	.04	.73	.39
Total aldehydes	.007	.50	.30
Total ppm hydrocarbon	.07	.84	.18
Total reactive grams (ethylene equivalents)	.10	.75	.16

[1] The square of multiple correlation coefficient.

[2] Model I: $Y = a_1$ (paraffins) + a_2 (olefins) + a_3 (aromatics),

Model II: $Y = a_1$ (paraffins) + a_2 (olefins) + a_3 (aromatics) + a_4 (car_6) + a_5 (car_7) + a_6 (car_9) + a_7 (car_{10}),

Model III: $Y = a_1$ (paraffins) + a_2 (olefins) + a_3 (aromatics) + a_4 (A/F).

Presence of "car effect" is interpreted to mean that the same fuel may yield different exhaust hydrocarbon mixtures in different automobiles. This raises the question, then, whether a change in fuel composition would have different effects on the exhaust from different automobiles. Such a

nonuniform fuel effect, in the language of statistics, is referred to as car-fuel interaction effect and is represented by the car-fuel product terms in the following statistical model:

$$(\text{Exh. component})_i = a_1 \times \text{fuel}_1 + \ldots + c_1 \times \text{car}_1 + \ldots + k_1 \text{ fuel}_1 \times \text{car}_1 + \ldots$$

Statistical analysis of the data from the first phase of the multiple-vehicle program showed that the car-fuel interaction effect was small, suggesting, that a change in fuel composition would have equal effects on exhaust from different automobiles. This finding is useful in that it suggests that in studying the effect of fuel composition on hydrocarbon emissions, use of a large number of test automobiles may be unnecessary.

Smog Chamber Program

Results from the smog chamber program are given in table 8. The most significant observations from these results are that the exhaust samples tested did not show large differences in reactivity in spite of the great diversity in fuel composition. In fact, from plots of exhaust reactivity against fuel aromatics (fig. 3),[7] the dependence of reactivity on fuel aromatics did not seem to be as strong as previous studies in this laboratory had suggested (fig. 4, dark circles). In view of the importance of the issue regarding the effect of fuel aromatics on exhaust reactivity, the data from this program were scrutinized in searching for information relevant to this issue. Thus, we explored the possibility, suggested by the multiple-car tests that exhaust reactivity depends on levels of some, but not the total of all, fuel aromatics. Results showed that exhaust reactivity, indeed, appears to be more strongly dependent on polyalkylbenzenes (fig. 5), than on total aromatics in fuel. This finding, consistent with the fleet testing results from the multivehicle tests probably establishes the relatively high pollution potential of polyalkylbenzenes in fuel. However, the effect of the polyalkylbenzenes on exhaust reactivity does not alone explain the unusually large differences in exhaust reactivity that were observed for some of the fuels in the earlier Bureau of Mines study (3).

[7] Exhaust reactivity in this and following figures is expressed in units of molar propylene equivalents; that is, in units of reactivity of an equimolar concentration of propylene.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21

Fuel No.	Initial chamber concentrations			Reactivity data								
	HC_i, ppmC	NO_{2_i}, ppm	HC/NO_x	R_{NO_2}, ppb/min	Maximum, ppm				Dosages, ppm × min			
					O_3[1]	PAN	PPN	HCHO	O_3[1]	PAN	PPN	HCHO
	6 ppmC:1 ppm NO_x											
1.....	6.02	0.102	6.05	13.01	0.92	0.094	0.017	0.76	134	14.25	2.60	202
	6.06	.105	6.10	12.88	.90	.099	.017	.81	134	14.91	2.69	198
	5.88	.111	5.54	14.28	.97	.129	.024	.78	163	20.73	3.63	211
	5.90	.099	5.84	13.73	.85	.102	.019	.84	149	17.21	3.22	226
2.....	6.07	.089	6.04	11.86	1.03	.101	.015	.72	151	14.66	2.10	195
	6.06	.107	6.05	14.85	.96	.117	.021	.88	166	19.62	3.53	195
	5.96	.102	5.92	15.41	.98	.118	.022	.84	182	21.53	3.86	217
	5.87	.106	5.77	15.04	.83	.113	.020	.74	143	19.81	3.34	202
	6.05	.101	5.99	11.97	.91	.089	.021	.66	133	13.06	3.04	177
	6.07	.107	5.97	12.49	.98	.086	.019	.68	147	13.23	3.07	178
3.....	6.08	.103	5.86	11.66	.98	.073	.013	.64	136	10.63	1.93	166
	6.09	.105	6.01	12.32	1.04	.077	.015	.96	152	12.14	2.31	232
	5.92	.103	5.84	13.45	.94	.114	.020	.73	156	18.93	3.46	183
	6.09	.098	5.98	14.30	.90	.117	.022	.87	165	20.97	3.91	215
4.....	6.00	.099	5.90	12.90	1.02	.083	.018	.65	159	13.27	2.72	175
	6.27	.109	6.30	13.27	.94	.122	.025	.72	139	18.10	3.80	187
	6.07	.107	5.90	15.39	.96	.120	.025	.67	171	21.56	4.38	173
	6.20	.110	5.96	14.93	.87	.121	.026	.75	160	21.32	4.51	199
5.....	6.06	.105	6.10	13.12	1.08	.116	.021	.76	194	19.41	3.49	209
	6.05	.106	6.03	11.84	.96	.114	.024	.81	152	17.66	3.75	202
	6.11	.095	6.05	13.25	.97	.102	.023	.90	153	15.87	3.43	206
	6.03	.095	6.25	12.30	.87	.123	.029	.81	142	19.12	4.32	208
	6.04	.097	5.93	11.81	.90	.097	.022	.66	134	14.19	3.35	168
	6.06	.089	6.14	10.23	.86	.089	.024	.65	119	13.86	3.43	158
	6.01	.092	5.87	11.01	.89	.074	.017	.62	127	10.61	3.39	154
	6.03	.095	5.98	11.35	.86	.106	.026	.66	123	15.23	3.84	170
	6.04	.108	5.94	11.92	.86	.091	.027	.74	127	13.17	3.97	201
	6.05	.114	6.58	10.77	.92	.100	.028	.72	146	15.42	4.20	196
	6.06	.103	6.04	11.51	.88	.087	.025	.67	126	12.57	3.56	178
6.....	6.02	.101	5.90	11.87	1.04	.066	.016	.88	146	10.15	2.15	209
	6.04	.101	5.86	11.58	1.01	.081	.014	.79	140	12.74	2.13	194
	6.00	.104	5.88	12.36	.95	.091	.019	.84	142	13.46	2.72	224
	6.15	.102	6.18	12.38	.84	.101	.021	.84	132	15.38	3.13	210
7.....	6.04	.088	6.00	11.09	.73	.058	.013	.68	96	7.23	1.66	188
	5.97	.092	5.93	11.11	.70	.058	.012	.65	95	8.77	1.80	187
	6.01	.094	6.18	11.04	.81	.082	.018	.66	113	10.94	2.30	182
	6.09	.098	6.04	11.17	.87	.079	.016	.76	121	10.87	2.17	217

[1]Measured with the chemiluminescence ozone detector.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21--Continued

Fuel No.	Initial chamber concentrations			Reactivity data								
	HC_i, ppmC	NO_{2_i}, ppm	HC/NO_x	R_{NO_2}, ppb/min	Maximum, ppm				Dosages, ppm X min			
					O_3[1]	PAN	PPN	HCHO	O_3[1]	PAN	PPN	HCHO
6 ppmC:1 ppm NO_x--Continued												
8.....	5.98	0.096	5.88	12.47	0.87	0.088	0.015	0.56	130	12.92	2.27	147
	5.99	.091	5.94	10.96	.89	.091	.016	.61	137	14.99	2.58	157
	6.02	.096	5.99	11.52	.84	.088	.014	.61	125	13.51	2.43	159
	6.04	.100	5.83	11.54	.88	.098	.018	.58	136	15.20	2.64	153
	6.05	.103	6.02	10.42	.88	.106	.02	.59	126	15.62	2.71	159
9.....	6.00	.104	6.02	11.57	.89	.088	.018	.85	136	13.75	2.68	203
	6.00	.101	5.93	11.94	.88	.092	.017	.69	128	13.50	2.44	174
	6.09	.098	6.05	11.86	.91	.103	.02	.78	140	15.38	2.99	195
	6.06	.096	6.13	10.26	.84	.083	.016	.66	113	11.89	2.21	176
10.....	5.99	.089	6.07	10.37	.78	.060	.009	.63	103	9.29	1.44	153
	6.01	.086	5.62	10.60	.69	.055	.009	.55	86	8.47	1.26	141
	5.96	.100	6.03	9.44	.72	.072	.010	.58	93	9.56	1.29	141
	5.99	.087	5.73	9.13	.66	.058	.010	.57	79	8.31	1.16	154
11.....	6.16	.104	6.14	11.44	.94	.116	.013	.74	152	18.97	2.16	160
	6.03	.106	5.88	12.70	.96	.120	.014	.66	163	20.26	2.18	157
	6.08	.103	6.02	12.58	.85	.122	.013	.65	158	21.75	2.32	183
12.....	6.03	.102	6.03	11.5	.68	.07	.007	.55	92	10.23	.97	152
	5.93	.101	5.94	11.8	.74	.07	.007	.59	102	9.77	1.05	164
	5.97	.109	5.92	11.4	.63	.06	.006	.54	83	9.03	.89	159
13.....	6.01	.091	6.40	10.3	.60	.05	.006	.64	72	6.44	.76	191
	5.95	.099	5.88	9.7	.52	.04	.005	.72	58	5.20	.65	185
14.....	6.03	.100	5.59	10.9	.80	.10	.008	.77	107	13.87	1.07	200
	5.97	.103	5.83	12.5	.93	.11	.008	.67	135	15.56	1.18	182
15.....	6.05	.099	5.81	11.2	.81	.10	.006	.71	111	13.66	.86	185
	6.00	.104	5.89	10.8	.93	.09	.006	.48	125	12.92	.75	119
16.....	5.98	.101	5.93	10.5	.64	.06	.003	.60	76	7.79	.43	176
	6.00	.104	5.95	10.3	.63	.05	.003	.58	73	6.32	.34	154
17.....	6.05	.105	5.92	11.5	.68	.08	.013	.62	90	10.58	1.61	169
	6.08	.103	6.12	11.3	.79	.07	.010	.79	102	9.29	1.39	164
18.....	6.05	.100	5.85	10.6	.67	.06	.003	.54	81	8.38	.38	149
	6.05	.105	5.92	9.5	.66	.05	.003	.45	77	6.83	.33	117

[1]Measured with the chemiluminescence ozone detector.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21--Continued

Fuel No.	Initial chamber concentrations			Reactivity data								
	HC_1, ppmC	NO_{2_1}, ppm	HC/NO_x	R_{NO_2}, ppb/min	Maximum, ppm				Dosages, ppm × min			
					O_3[1]	PAN	PPN	HCHO	O_3[1]	PAN	PPN	HCHO
6 ppmC:1 ppm NO_x--Continued												
19.....	6.00	0.103	6.00	10.3	0.61	0.05	0.006	0.60	75	6.59	0.75	160
	5.99	.103	5.90	11.0	.75	.05	.006	.52	95	6.73	.76	141
20.....	6.00	.100	5.98	11.2	.64	.06	.006	.71	78	7.49	.80	185
	6.01	.103	5.93	10.5	.70	.05	.006	.56	87	7.43	.80	159
21.....	6.07	.097	5.80	10.2	.69	.08	.007	.75	84	10.57	.98	167
	6.02	.100	5.99	10.5	.87	.08	.007	.52	111	11.42	.96	141
3 ppmC:1/2 ppm NO_x												
1.....	3.00	0.050	6.04	6.11	0.53	0.041	0.008	0.41	80	6.40	1.14	106
	3.02	.053	6.01	6.13	.68	.049	.009	.38	105	7.97	1.39	106
	3.00	.045	6.04	5.62	.54	.040	.008	.45	80	6.37	1.14	112
	2.96	.048	6.08	6.60	.63	.050	.010	.40	104	8.23	1.50	112
2.....	3.07	.048	6.38	5.62	.53	.040	.008	.33	80	6.65	1.17	89
	3.04	.046	5.94	6.36	.61	.047	.009	.33	95	7.70	1.47	84
	3.03	.048	6.46	5.95	.63	.051	.011	.47	101	8.69	1.72	113
	3.04	.045	6.24	6.40	.65	.057	.012	.40	107	9.64	1.88	108
3.....	3.06	.050	6.13	5.85	.56	.040	.008	.45	86	6.37	1.26	97
	3.02	.049	6.03	6.98	.68	.051	.010	.41	115	8.76	1.62	119
	3.00	.045	6.17	6.76	.62	.049	.009	.42	105	8.54	1.58	109
	3.03	.044	6.19	6.11	.60	.049	.009	.40	96	7.88	1.36	109
4.....	3.04	.046	6.16	6.50	.64	.046	.011	.43	106	8.15	1.73	100
	3.03	.045	5.99	6.43	.62	.053	.013	.40	101	8.68	1.96	101
	3.02	.049	6.02	7.00	.62	.051	.011	.41	107	8.85	1.91	108
	3.02	.046	6.13	7.63	.69	.051	.011	.38	119	9.08	1.95	95
5.....	3.04	.046	6.02	7.19	.62	.047	.010	.56	102	7.96	1.73	114
	3.04	.050	6.23	6.46	.61	.046	.011	.33	97	7.29	1.66	80
	3.00	.047	5.99	6.21	.60	.046	.012	.35	94	7.34	1.68	104
	3.01	.048	6.29	6.48	.68	.051	.013	.38	114	8.68	1.96	108
6.....	2.93	.045	6.08	6.00	.63	.045	.010	.42	98	7.15	1.58	117
	2.99	.046	6.00	6.49	.62	.049	.010	.38	100	7.78	1.56	109
	3.02	.047	5.97	6.04	.61	.043	.009	.37	92	6.30	1.34	105
	3.03	.044	5.97	6.33	.61	.045	.010	.41	94	6.87	1.40	115

[1]Measured with the chemiluminescence ozone detector.

TABLE 8. - Smog chamber reactivities of exhaust from fuels 1-21--Continued

Fuel No.	Initial chamber concentrations			Reactivity data								
	HC_1, ppmC	NO_{2_1}, ppm	HC / NO_x	R_{NO_2}, ppb/min	Maximum, ppm				Dosages, ppm × min			
					O_3[1]	PAN	PPN	HCHO	O_3[1]	PAN	PPN	HCHO
	3 ppmC:1/2 ppm NO_x--Continued											
11.....	3.06	0.050	6.13	5.60	0.58	0.043	0.005	0.28	84	7.13	0.77	73
	2.98	.048	5.91	6.51	.66	.050	.006	.34	110	9.09	.93	95
	3.02	.047	6.26	5.28	.62	.045	.004	.39	93	7.45	.85	100
	3.00	.042	6.15	6.35	.63	.053	.006	.40	109	9.83	1.02	105
12.....	2.66	.049	5.40	6.55	.38	.023	.002	.48	61	3.43	.29	155
	3.01	.052	5.96	6.19	.47	.031	.003	.37	70	4.65	.44	103
13.....	3.04	.054	5.73	6.38	.42	.025	.003	.35	58	4.20	.36	97
	3.03	.053	6.17	6.19	.51	.037	.004	.43	78	5.61	.52	120
14.....	2.98	.053	5.96	6.58	.52	.049	.004	.33	82	7.93	.62	93
	3.01	.055	6.02	5.56	.54	.040	.004	.45	84	6.16	.56	122
15.....	3.01	.055	5.89	6.71	.56	.048	.003	.35	87	7.80	.44	100
	3.01	.059	6.15	6.40	.58	.045	.003	.34	97	7.24	.45	99
16.....	3.01	.059	5.98	6.32	.50	.034	.002	.36	73	5.02	.23	98
	3.00	.051	5.93	6.15	.48	.032	.002	.33	71	4.68	.21	109
17.....	3.01	.051	5.93	6.97	.53	.038	.006	.45	78	6.02	.81	127
	3.03	.050	6.05	6.12	.51	.036	.005	.46	76	5.31	.68	117
18.....	3.04	.054	6.08	6.21	.52	.037	.002	.38	77	5.74	.30	109
	3.03	.049	5.98	6.04	.54	.040	.002	.39	80	5.95	.29	104
19.....	3.01	.051	6.04	6.94	.55	.031	.004	.47	83	4.76	.51	130
	3.13	.055	6.12	6.99	.60	.042	.005	.49	94	6.29	.66	124
20.....	3.00	.056	5.90	6.74	.52	.038	.004	.39	78	5.94	.59	110
	3.07	.061	6.18	6.33	.53	.038	.004	.43	79	5.48	.54	112
	3.09	.054	6.19	5.42	.46	.036	.004	.41	65	5.02	.49	112
21.....	3.08	.054	5.94	6.35	.56	.044	.004	.41	83	6.84	.57	107
	3.06	.048	6.04	6.52	.56	.053	.005	.37	88	8.03	.68	103
	3.00	.055	5.78	5.76	.45	.039	.003	.37	66	5.78	.49	97

[1]Measured with the chemiluminescence ozone detector.

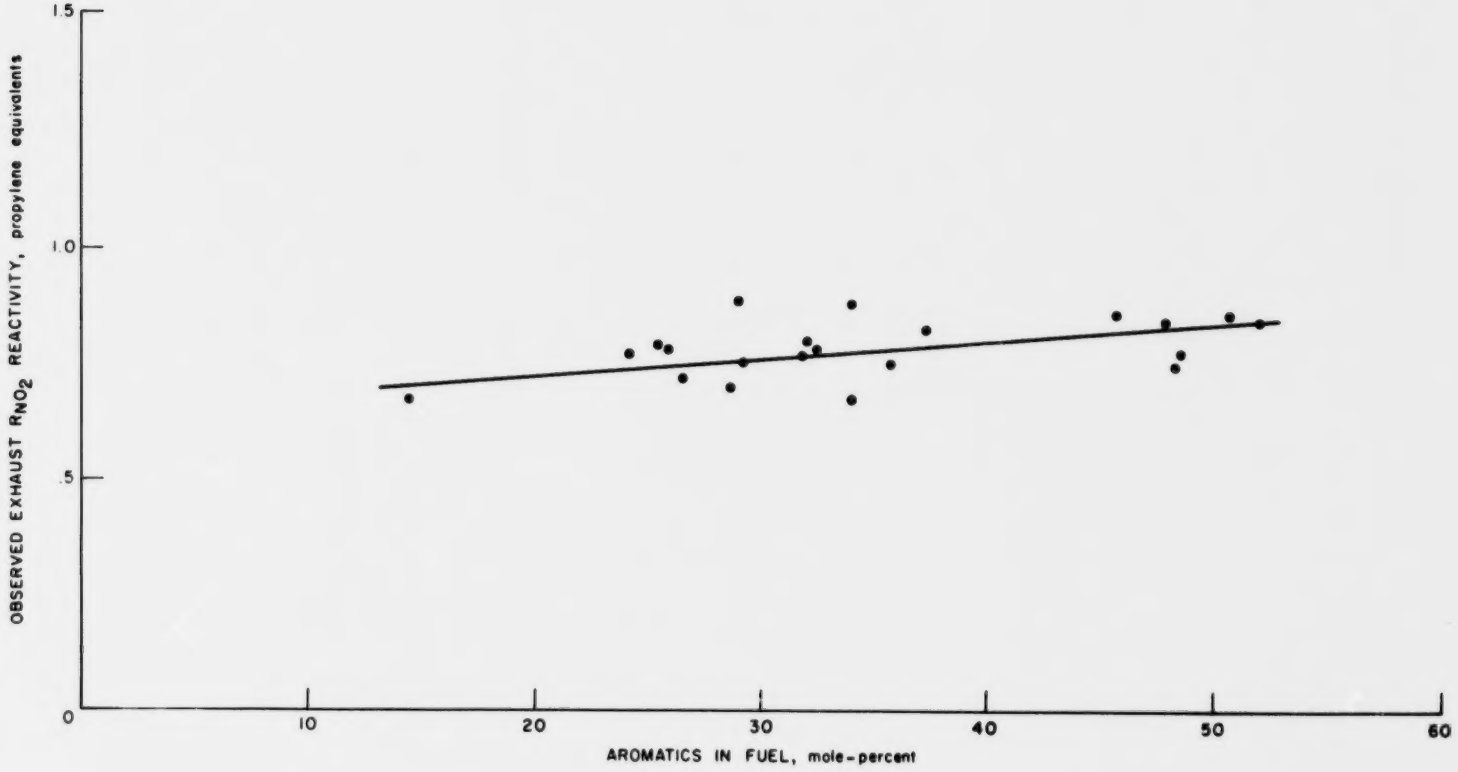

FIGURE 3. - Correlation of observed exhaust reactivities with total aromatic levels in fuel.

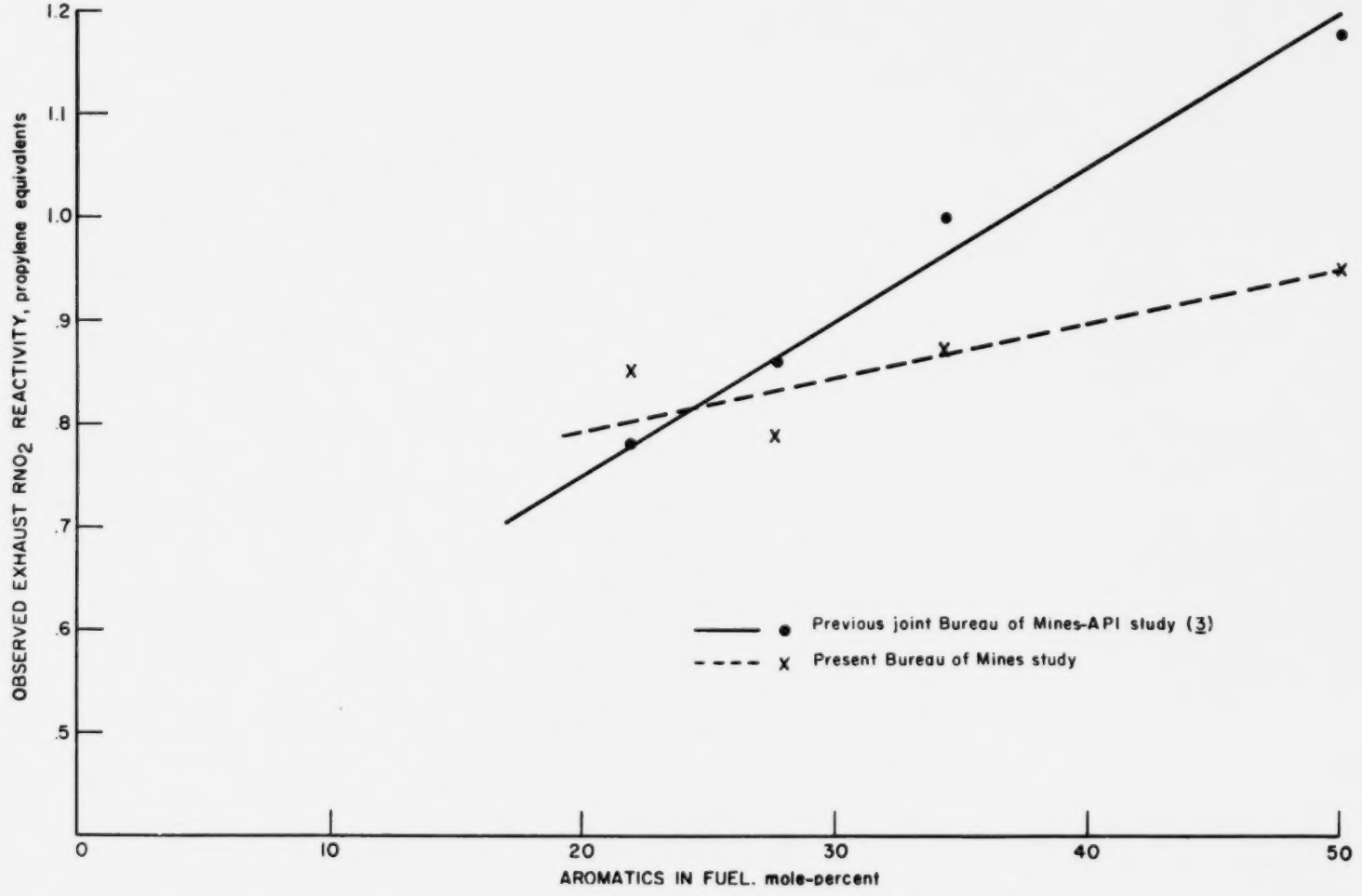

FIGURE 4. - Comparison of exhaust reactivites–fuel aromatic relationships from two Bureau of Mines studies.

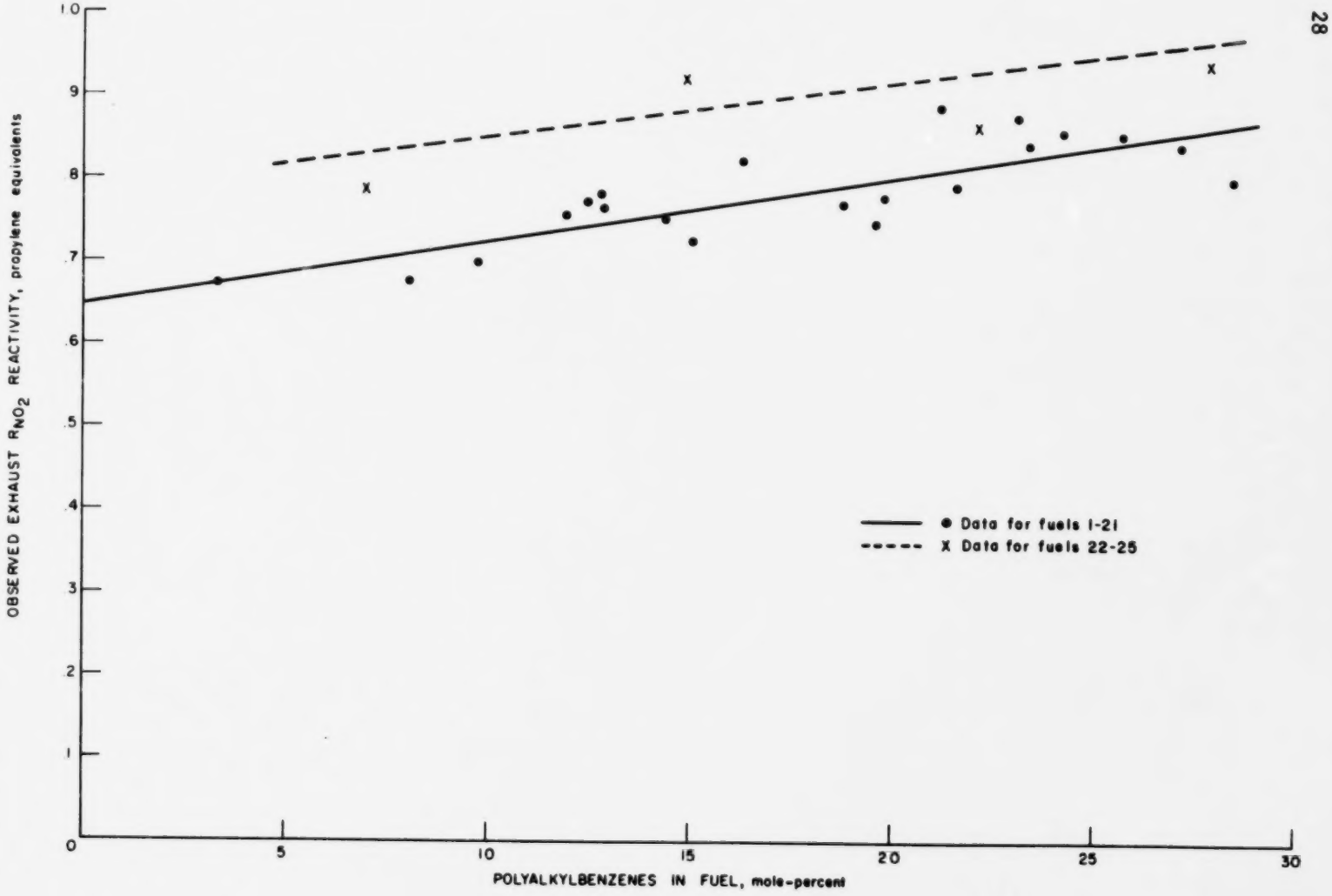

FIGURE 5. - Correlation of observed exhaust reactivities with polyalkylbenzene levels in fuel.

In attempting to understand the differences in results between this and the earlier Bureau of Mines studies regarding effect of fuel aromatics on exhaust reactivity, the possibility was explored that experimental error may account for part or all of the difference in question. To this end, the data from this study was fitted to the exhaust reactivity--exhaust composition correlation equation developed in the earlier study. Figure 6 shows the curve depicting that correlation equation along with the scatter boundaries and the correlation data (dots) obtained in the present study. The excellent agreement between the correlation points of the two studies suggests that the quality of experimental data (smog chamber reactivity and chromatographic analysis

FIGURE 6

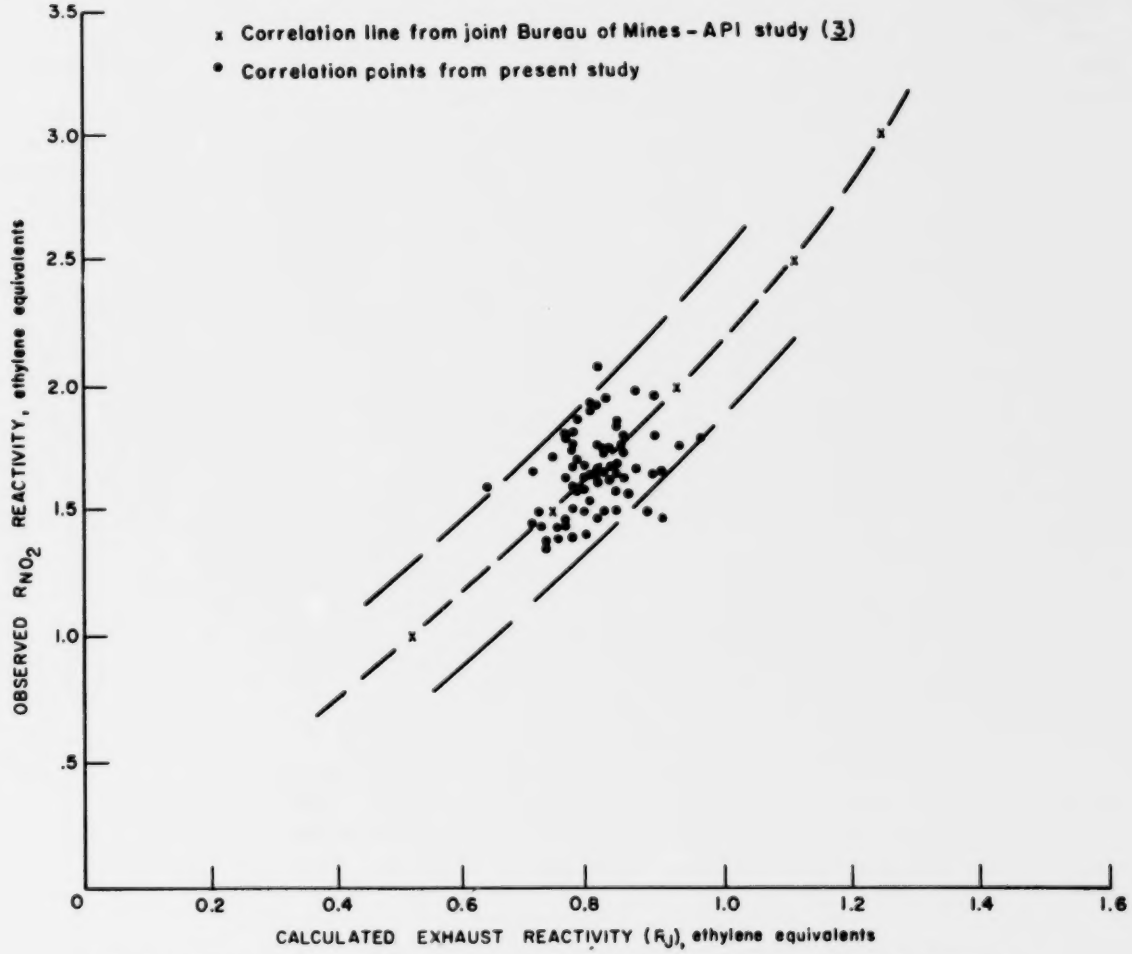

FIGURE 6.- Correlation of Observed and Calculated (Jackson Scale) Exhaust R_{NO_2} Reactivities.

FIGURE 6. - Correlation of observed and calculated (Jackson scale) exhaust R_{NO_2} reactivities.

data on exhaust hydrocarbons) was about the same for the two studies. This would discredit experimental error as the sole cause of the difference in results between the earlier and the present studies. Finally, to determine whether differences in test conditions can account for these differences, the fuels of the earlier Bureau of Mines study (fuels 22-25, table 1) were tested again; this time using the experimental automobile and conditions of the present study. Retesting included chromatographic analysis of fuels since the present fuel samples were taken from a new batch that might differ somewhat in composition from the fuel batch used in the earlier study. Results of the reactivity observations given in table 9 did show a trend of increasing reactivity with increasing levels of fuel aromatics (see fig. 4, crosses) but this trend was not as strong as that that was observed in the earlier study (fig. 4, dots). It was, therefore, deduced that the differences in results between this and the earlier fuel studies were caused, partly at least, by differences in test conditions.

TABLE 9. - Smog chamber reactivities of exhaust from fuels 22-25

Fuel No.	Initial chamber concentrations			Reactivity data								
	HC_i, ppmC	NO_{2_i}, ppm	HC/NO_x	R_{NO_2}, ppb/min	Maximum, ppm				Dosages, ppm × min			
					O_3[1]	PAN	PPN	HCHO	O_3[1]	PAN	PPN	HCHO
	6 ppmC:1 ppm NO_x											
22.....	5.96	0.099	5.92	10.5	0.68	0.07	0.008	0.72	87	9.48	1.12	189
	6.05	.104	6.06	10.8	.62	.06	.008	.67	72	8.26	.98	177
23.....	6.01	.103	5.97	12.4	.80	.09	.012	.75	122	13.71	1.74	192
	6.02	.102	6.04	11.6	.75	.09	.012	.89	106	13.17	1.19	204
24.....	6.04	.104	5.97	10.9	.71	.10	.008	.67	101	14.44	1.15	174
	6.04	.109	5.95	10.7	.77	.12	.010	.62	115	18.28	1.54	166
25.....	6.05	.100	6.13	12.7	.71	.08	.011	.68	102	12.44	1.58	190
	5.96	.101	5.97	10.9	.72	.10	.011	.71	99	14.62	1.69	204

[1]Measured with the chemiluminescence ozone detector.

In attempts to associate exhaust reactivity with nonaromatic fuel components, reactivities were plotted versus total olefins, internal olefins, n-paraffins, and isoparaffins in fuel for constant total aromatic or total polyalkylbenzenes. With one exception, no systematic patterns could be observed in these plots, suggesting that composition differences within the groups of olefins, n-paraffins, and isoparaffins are probably causing some differences in exhaust reactivity. The exception was the apparent correlation between peroxypropionyl nitrate (PPN) yields in the irradiated exhaust and the level of olefins in the fuel. Note that peroxyacetyl nitrate (PAN) yields did not show the same trend. This might suggest that PPN results mainly from fuel olefins surviving in the exhaust rather than from olefins that result from the combustion process and yield primarily PAN.

An alternative approach to relating exhaust reactivity with fuel composition is through intermediate correlation with exhaust composition. Application of this approach was illustrated in the American Petroleum Institute study (of the effect of fuel composition on exhaust reactivity) (3). Briefly, the approach entails statistical treatment of exhaust composition and exhaust reactivity data to develop a reactivity-composition correlation equation. Using such an equation upon the data from the multiple-vehicle tests, exhaust reactivities are obtained from exhaust compositions and are subsequently correlated with fuel composition. In the present study this approach did not appear promising at first, primarily because exhaust reactivity did not correlate well with exhaust composition. Part A of figure 7 depicts this correlation using as measure of exhaust composition the "linear summation reactivity" value obtained from exhaust composition and Jackson specific reactivity data (8). Part B of figure 7 depicts the same correlation, except that here linear summation reactivity values were calculated from Bureau of Mines specific reactivities as shown in table 10 rather than Jackson reactivities. Use of the specific reactivities shown in this table did improve the correlation but not to the point of providing a usable correlation equation. This lack of strong correlation in the data of this study was attributed to the narrow range within which the correlation variables (exhaust reactivity and exhaust composition) were included.

TABLE 10. - Bureau of Mines rate-of-NO_2-formation reactivity scale[1]

Exhaust component or group	Bureau of Mines specific R_{NO_2} reactivity in propylene equivalents	Exhaust component or group	Bureau of Mines specific R_{NO_2} reactivity in propylene equivalents
Ethylene	0.47	R-benzyls[3]	0.49
Propylene	1.00	R-nonbenzyls[4]	.45
1-Alkenes	.65	R_x-benzenes[5]	1.19
Int-Alkenes	3.78	Formaldehyde	.79
Diolefins	1.41	Aliphatic aldehydes	1.41
C_{4+} Paraffins[2]	.18	o-Tolualdehyde	5.98
Benzene	.15	Aromatic aldehydes	.19

[1] Smog chamber experiments involving several typical exhaust aldehydes as reported in (5) and unreported results involving 19 typical exhaust hydrocarbons.
[2] Excludes methane, ethane, and propane.
[3] Includes toluene, ethylbenzene, n-propylbenzene, etc.
[4] Includes iso-propylbenzene, t-butylbenzene, etc.
[5] Includes the xylenes, mesitylene, and other polysubstituted benzenes.

The analysis of the smog chamber data thus far points to the same conclusion that was reached in tests with the 11 automobiles, namely: Differences in reactivity among exhausts from different fuels are not caused solely by differences in relative levels of paraffins, olefins, and aromatics in fuel; differences in composition within each of these hydrocarbon classes are also a factor.

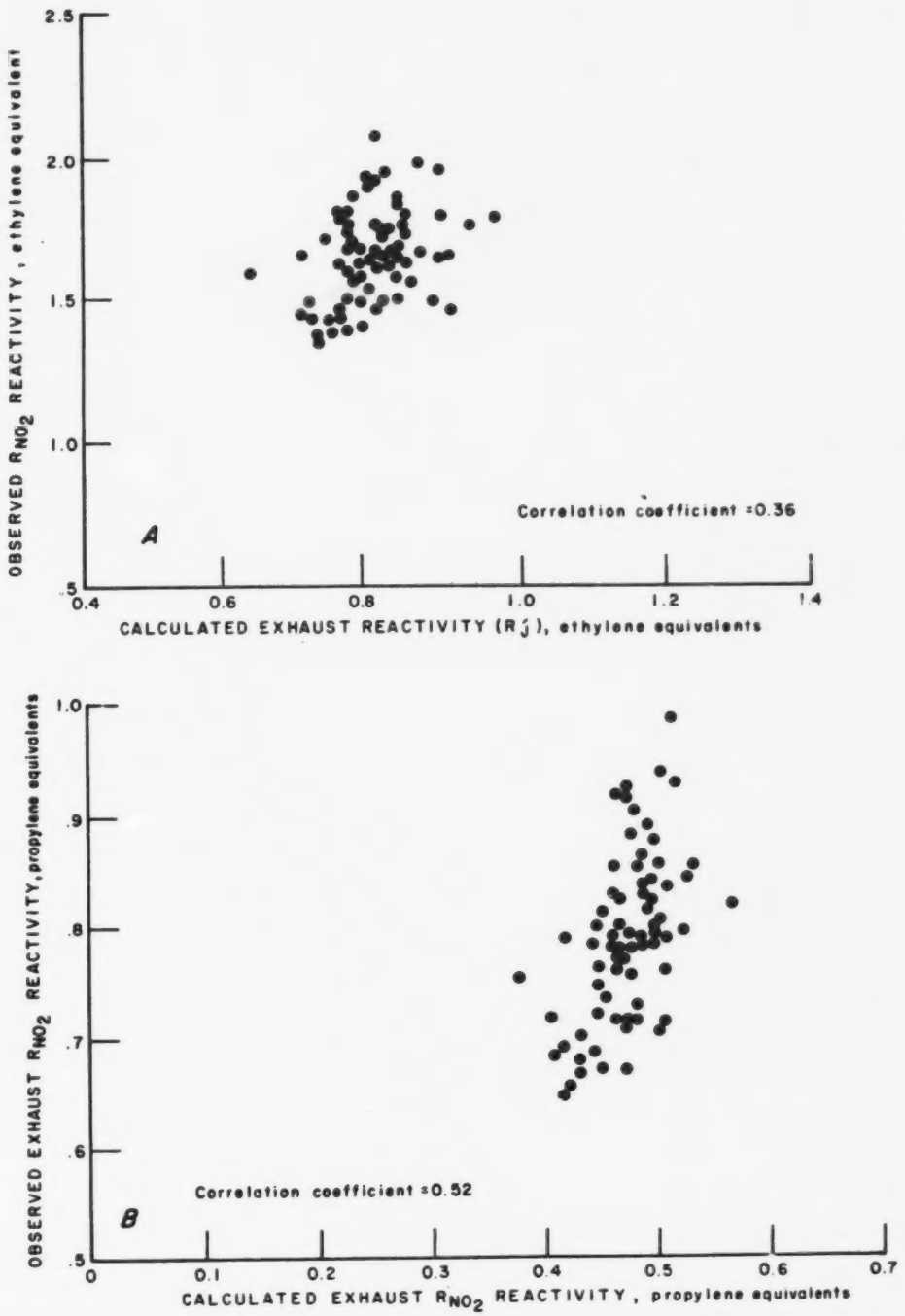

FIGURE 7. - Correlation of observed exhaust R_{NO_2} reactivities with calculated reactivities by Jackson and Bureau of Mines scales.

This conclusion led to the idea of attempting to correlate exhaust reactivity with fuel composition expressed in terms of individual component--rather than component group--data. The concept here entails development of a "fuel reactivity scale," that is, a rating system by which each fuel component would be rated according to its contribution to exhaust reactivity. Given those ratings or "specific reactivities" (r_i), and the mole fractions of the individual fuel components (x_i), exhaust reactivity (R_{exh}^{calc}) could then be calculated using the equation,

$$R_{exh}^{calc} = \Sigma x_i r_i .$$

The success of this method for correlating exhaust reactivity with fuel composition would be measured by the extent of agreement between the calculated (R_{exh}^{calc}) and observed (R_{exh}^{obs}) exhaust reactivity values.

In order to use this correlation method upon the data of this study, first specific reactivity values had to be assigned to the various fuel components. Several alternative sets of such assignments were made based on speculation and on the limited information available regarding automotive combustion of hydrocarbons. The set of assignments that gave the best predictions of exhaust rate-of-NO_2-formation reactivity was as follows: Except for paraffins, each fuel hydrocarbon was given a specific reactivity value equal to that assigned by Jackson (8); paraffins were given reactivity values equal to twice the corresponding Jackson value. The rationale of these assignments is based on the fact that reactive exhaust organics consist mainly of unburned fuel and of products from cracking of the aliphatic fuel components. Following these specific reactivity assignments, exhaust reactivity was calculated, and resultant values were compared to those for observed exhaust reactivity. Results are shown in figure 8. The correlation appears to be good despite the speculative character of the specific reactivity assignments made. This verifies the advantage of expressing fuel composition in terms of individual component data rather than in terms of broadly defined fuel component groups. Interestingly, exhaust reactivity did not correlate as well with exhaust composition (see Part A of fig. 7) as it did with fuel composition (fig. 8). This is probably due to relatively large experimental errors in the chromatographic measurement of exhaust composition; error in chromatographic measurement of fuel composition is much smaller.

Influence of Engine Air-Fuel Ratio (A/F) on Correlation Results

Operating the test automobile used in the smog chamber program with fuel-enriched A/F raised questions regarding validity of results and prompted a brief investigation of the effect of A/F on reactivity of exhaust emissions. Data for this investigation were obtained both in the simple hydrocarbon fuel testing program of this study and in another study in which a 1963 Chevrolet engine, 283-cu-in displacement (CID), was operated under varied A/F conditions using gasoline fuels of various compositions. The data from the simple fuel tests (discussed also in the following section of this report), plotted in figure 9, showed the A/F to have a nonuniform effect on exhaust reactivity. Thus, with the paraffin fuels, the A/F effect was strong in the fuel-rich region and weak in the fuel-lean region, and its magnitude varied only

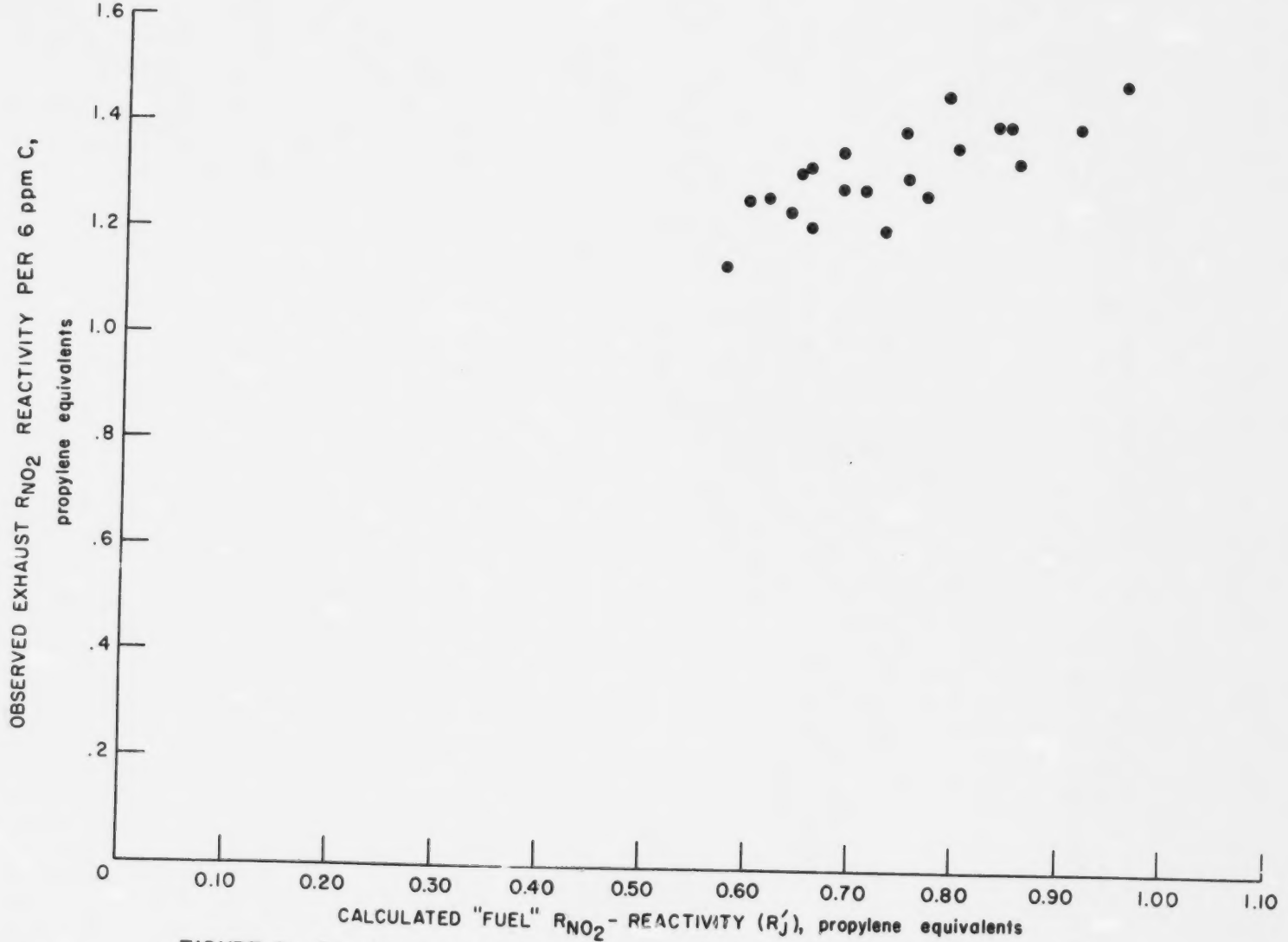

FIGURE 8. - Correlation of observed exhaust reactivities with calculated "fuel" reactivities.

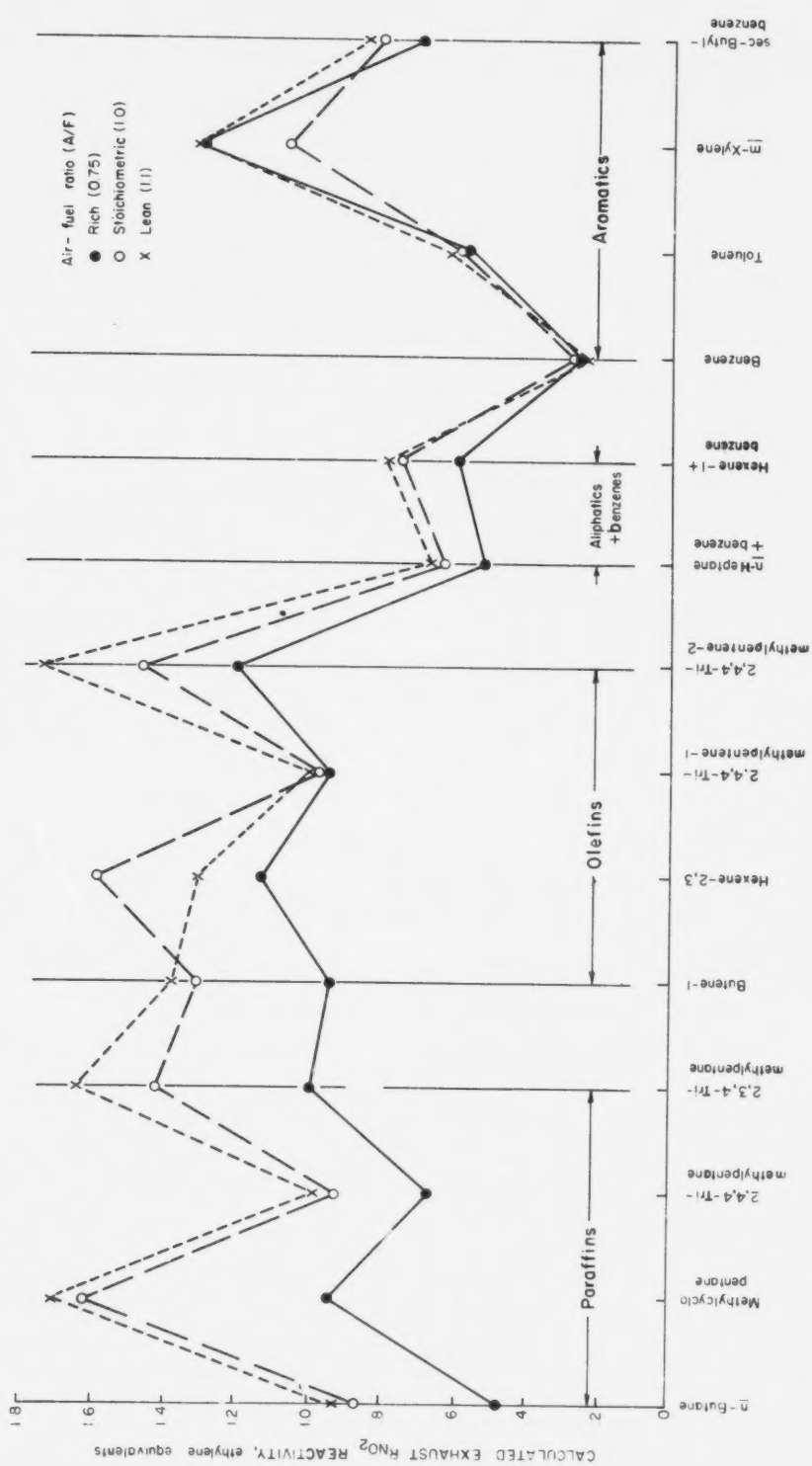

FIGURE 9. - Calculated R_{NO_2} reactivities of exhaust from simple hydrocarbon fuels used under varied A/F conditions.

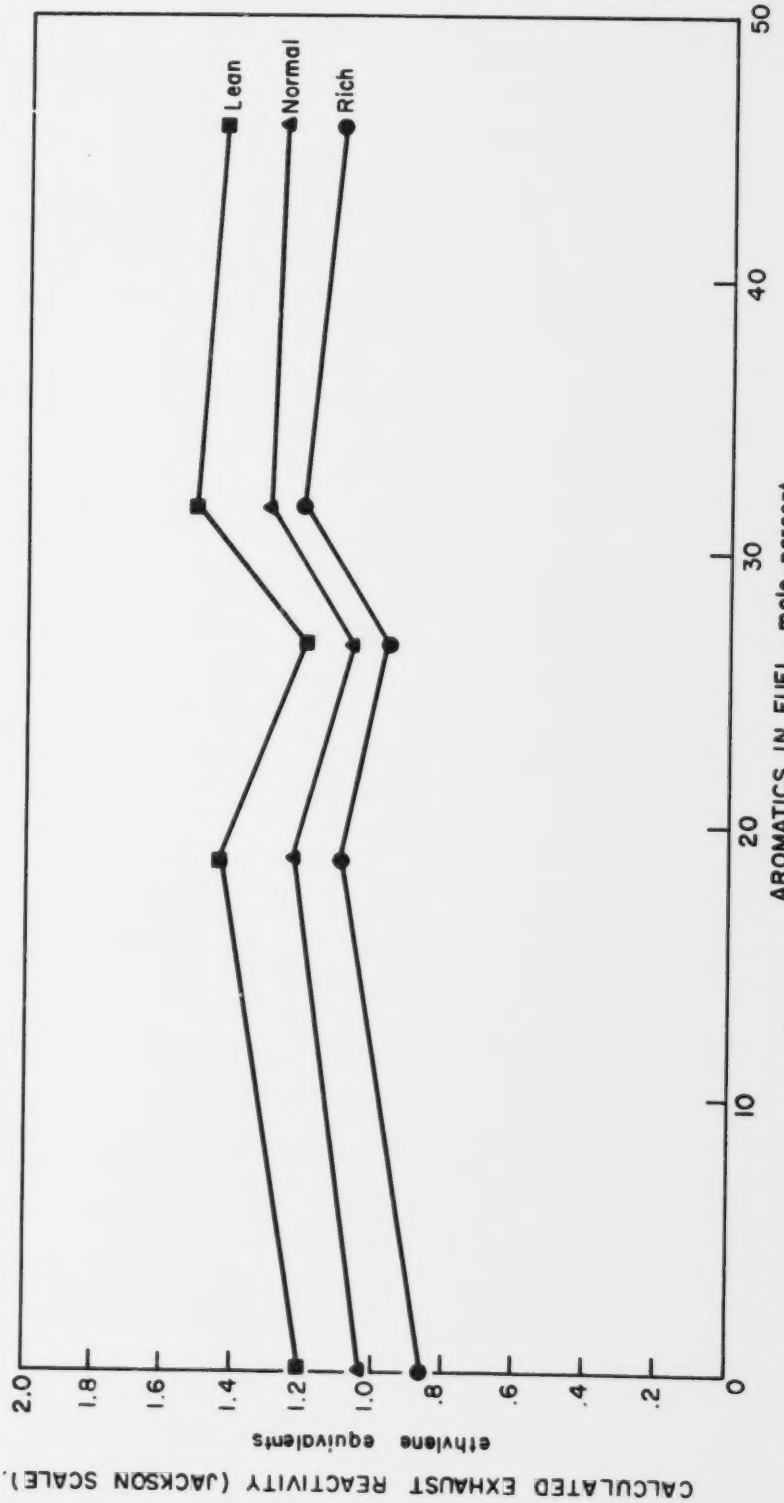

FIGURE 10. - Calculated R_{NO_2} reactivities of exhaust from gasoline fuels used under varied air-fuel ratio conditions.

moderately from fuel to fuel. With the aromatic fuels, the A/F effect was generally weak throughout the A/F range used. With the olefin fuels, the A/F effect was strong, and its magnitude varied considerably from fuel to fuel. These data suggest that with gasolines the A/F effect may vary in magnitude from fuel to fuel depending on aromatic and olefin content.

More direct information on the effect of A/F on gasoline exhaust reactivity was provided by the tests with the Chevrolet engine. Results from these tests are shown in figure 10. These results indicate that although changes in A/F affect exhaust reactivity, the changes affect the exhaust from different fuels in the same manner, preserving the relative order of their reactivities and, therefore, preserving relative fuel effects on exhaust reactivity. This finding, in turn, suggests that fuel enrichment of the A/F, necessary for acceptable HC/NO_x in exhausts produced for the smog chamber study, does not invalidate the conclusions from the study regarding the effect of fuel composition on exhaust reactivity.

Automotive Combustion of Simple Hydrocarbon Fuels

Results from the simple hydrocarbon fuel tests are given in table 11, and observed exhaust reactivity data are summarized in table 12. Note that these data represent specific reactivity of exhaust, that is, reactivity per mole of exhaust hydrocarbon, and they should be looked at solely as indicative of the nature of the exhaust organics that originate from the various fuel components. Data for the n-heptane and hexene-1 fuels could not be obtained directly because these hydrocarbons, having extremely low octane number, could not be used alone. The exhaust reactivity values listed in table 12 for these two hydrocarbons represent only gross estimates. They were obtained from comparison of data from the heptane and hexene-1 mixtures with aromatics versus data from the aromatics alone.

Regarding the main objective of these tests, the data of table 12 show that fuel hydrocarbons of varying structure yield exhaust of widely varying reactivity. The data support deductions drawn from the other segments of this study that for purposes of predicting exhaust reactivity, the simple classification of fuel hydrocarbons into paraffins, olefins, and aromatics is clearly inadequate. Further, the data confirms that structural differences within each of the constituent groups have equal or greater effect on exhaust reactivity than do the differences group-to-group. Although the present data are not sufficient to permit a fully adequate classification of fuel hydrocarbons, they nevertheless are suggestive of certain trends. Thus, normal paraffins appear to yield exhaust of relatively low reactivity, whereas cycloparaffin fuel yields exhaust considerably more reactive. Isoparaffin fuels may vary considerably in (exhaust) reactivity, evidently, depending on their molecular structures. Olefins of various molecular structure seem to yield exhaust of widely varying R_{NO_2} reactivity but of almost constant ozone-yield reactivity. Aromatic fuels of differing aromatic makeup also yield exhaust of widely varied reactivity, the polyalkylbenzenes appearing to yield exhaust that is considerably more reactive than the exhaust produced from monoalkylbenzenes and benzene. The data from the tests with the n-heptane mixtures (table 12) suggest also that the pollution potentials of the various hydrocarbons are

preserved when these hydrocarbons are used in mixture with others; evidently there are no strong synergistic effects in this respect.

TABLE 11. - Composition and smog chamber reactivities of exhaust from simple hydrocarbon fuels

Fuel	Concentrations in raw wet exhaust, ppm			Jackson reactivity, propylene equivalents	EPA[1] reactivity, propylene equivalents	Chamber reactivity, propylene equivalents	
	Hydrocarbon	Formaldehyde	Total aldehydes			R_{NO_2}	Maximum O_3
n-Butane	1,058	14.3	22.8	0.24	0.22	0.43	0.16
	1,369	15.2	21.8	.23	.22	.42	.18
n-Heptane + benzene	879	12.3	29.7	.24	.23	.59	.15
	925	12.3	36.8	.26	.23	.58	.16
2,4,4-Trimethylpentane	960	8.1	22.1	.32	.30	.53	.36
	1,260	17.1	28.8	.25	.24	.48	.29
2,3,4-Trimethylpentane	1,122	17.8	31.7	.51	.34	.78	.63
	1,177	14.4	27.7	.46	.31	.76	.61
Methylcyclopentane	913	8.8	24.2	.47	.27	1.00	.37
	999	11.2	16.1	.44	.26	.94	.33
Butene-1	1,085	20.4	39.3	.48	.51	.66	.66
	1,400	19.5	26.2	.44	.47	.57	.59
Hexene-1 + benzene	960	16.2	26.2	.30	.33	.58	.29
	1,099	12.1	19.5	.28	.31	.54	.33
2,4,4-Trimethylpentene-1	1,089	17.7	40.0	.47	.48	.75	.74
	1,371	20.5	41.0	.46	.47	.83	.73
Mixed 2- and 3-hexenes	1,134	23.4	51.6	.58	.47	.94	.66
	1,227	19.1	43.2	.53	.45	.89	.58
2,4,4-Trimethylpentene-2	1,090	14.0	36.7	.61	.40	1.86	.75
	1,234	23.1	36.7	.57	.38	1.78	.71
Benzene	723	8.5	14.3	.13	.06	.67	.03
	939	10.1	15.6	.12	.06	.66	.02
Toluene	703	7.3	17.2	.30	.31	.87	.36
	755	7.1	17.9	.28	.29	.87	.35
	857	4.5	14.9	.27	.29	.84	.31
sec-Butylbenzene	736	12.3	28.9	.35	.29	.84	.23
	862	12.7	35.1	.32	.27	.79	.23
m-Xylene	587	5.9	22.6	.65	.54	1.57	1.33
	806	3.7	11.6	.64	.53	1.55	1.39
n-Heptane + toluene	989	13.9	36.5	.29	.30	.67	.41
n-Heptane + m-xylene	987	8.1	22.8	.42	.38	.97	.92
n-Heptane + 2,4,4-trimethylpentene-2	1,520	20.5	41.0	.44	.34	1.01	.70

[1]Calculated using the EPA reactivity scale normalized to propylene reactivity = 1.0.

TABLE 12. - Summary of smog chamber reactivities of exhaust from simple fuels

Fuel	Reactivity, propylene equivalents	
	R_{NO_2}	Maximum O_3
n-Butane	0.4	0.2
n-Heptane	[1].5	[1].4
2,2,4-Trimethylpentane	.5	.3
2,3,4-Trimethylpentane	.8	.6
Methylcyclopentane	1.0	.4
Butene-1	.6	.6
Hexene-1	[1].5	[1].6
2,4,4-Trimethylpentene-1	.8	.7
Hexene-2,3	.9	.6
2,4,4-Trimethylpentene-2	1.8	.7
Benzene	.7	.0
Toluene	.9	.3
sec-Butylbenzene	.8	.2
m-Xylene	1.6	1.3
n-Heptane + toluene	.7	.4
n-Heptane + m-xylene	1.0	.9
n-Heptane + 2,4,4-trimethylpentene-2	1.0	.7

[1] Gross estimates obtained from comparison of data from the n-heptane mixtures with aromatics versus data from the aromatics alone.

Another interesting observation from these data pertains to the degree of agreement between observed and calculated reactivity values for exhaust from simple fuels. Figure 11 illustrates the degree of agreement between observed R_{NO_2} reactivity of exhaust and reactivity calculated from GLC-composition of exhaust and the Jackson reactivity scale (8). Observed reactivity values are considerably higher than the calculated ones. Note that the calculated reactivity value does not include the reactivity contribution of formaldehyde and a portion of the contributions of the heavier aldehydes. This is because the flame ionization detector used in the GLC method does not respond to formaldehyde and has relatively low response to the heavier aldehydes (5). Nevertheless, levels of aldehydes, as measured by the chromotropic acid and MBTH methods, are too low (see table 11) to affect noticeably the difference between observed and calculated reactivities.

These differences between observed and calculated reactivities have been noticed previously (3); however, the present data provide a somewhat more precise definition of this problem. Thus, for exhaust from aromatic fuels and for relatively more reactive exhaust the difference between observed and calculated reactivities is larger than for the rest of the exhaust samples of this study. This explains the large amount of scatter observed in correlations of observed and calculated reactivities of exhaust from fuels of varying aromatic contents (see fig. 7). The cause of this problem is not known. Nevertheless, based on experiences in this laboratory, these investigators speculated that the higher-than-expected reactivity of exhaust is caused, partly at

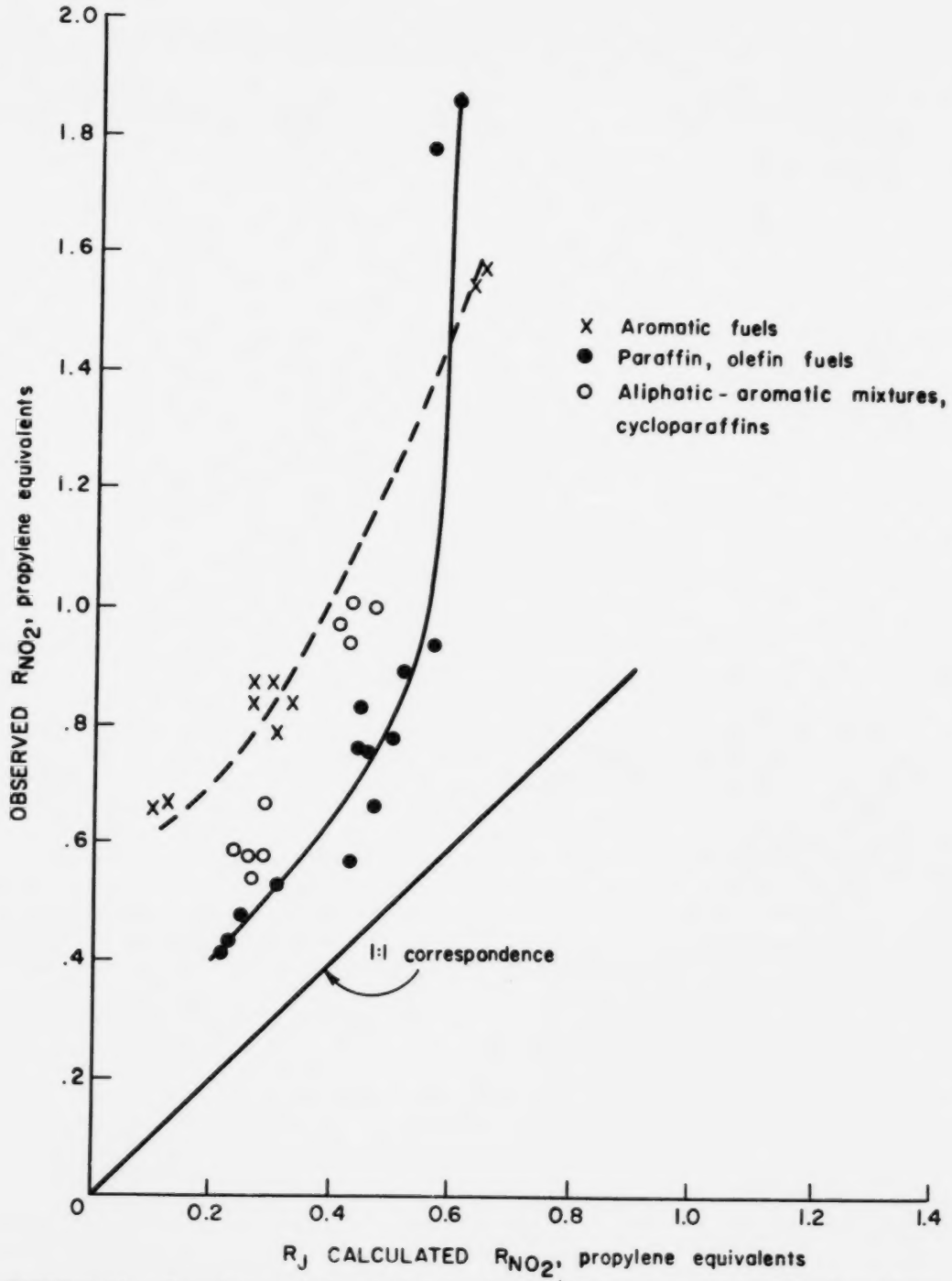

FIGURE 11. - Correlation of observed and calculated R_{NO_2} reactivities of exhaust from simple hydrocarbon fuels.

least, by reactive exhaust organics that have been totally missed or misidentified by sampling and the chromatographic method of exhaust analysis (5). The data from the present study underscore once again the unreliability of the "calculation" method as it is often used to estimate reactivity of exhaust emissions.

SUMMARY AND CONCLUSIONS

In efforts to associate automotive fuel composition with reactivity of exhaust emissions, a number of fuels of varied composition were tested using several automobiles operated with standard engine adjustments. The one investigative approach, exhaust reactivity, was calculated using a reactivity scale and exhaust composition data. Such calculated exhaust reactivity was then statistically correlated with fuel composition expressed using each of several different component classification schemes. Results showed that correlations were improved when compositional detail was added to the simple classification as paraffins, olefins, and aromatics. A similar conclusion was reached when levels of selected reactive exhaust components were statistically correlated with fuel composition. Further, from the fuel component groups considered, the group of polyalkylbenzenes was found to be the one that correlated best with calculated exhaust reactivity. The broader group of aromatics showed a weak correlation.

By an alternate investigative approach, fuel composition was correlated to exhaust reactivity that, instead of having been calculated, was measured experimentally using a smog chamber. For these smog chamber measurements the experimental fuels were tested using one automobile that was operated fuel-rich in order to yield exhaust with sufficiently high HC/NO_x ratio. Evidence was obtained in parallel to show that such operation of the test engine did not invalidate the findings from this smog chamber program. Findings in the smog chamber tests were essentially in agreement with those of the multiple-car tests. The failure to observe a strong effect of aromatics on exhaust reactivity contradicted indications from a previous study in this laboratory. In order to resolve or reduce the uncertainty posed by the differences, fuels used in the earlier study were retested under conditions of the present study. Results from this retesting did not provide a satisfactory explanation of the contradiction and the difference in question was attributed to differences in experimental conditions between the two studies.

The polyalkylbenzenes were the only fuel component group that were indicated by the correlations positively to have an influence on exhaust reactivity. Other components are, nonetheless, believed to have such an effect. Lack of strong correlation between exhaust reactivity and other fuel component groups, such as paraffins, isoparaffins, olefins, and internal olefins, was attributed to inappropriate definition of these groups. It is now indicated that to associate composition and exhaust reactivity, fuel composition should be expressed either (1) in terms of individual components or (2) in terms of component groups such that the potential for exhaust reactivity would be the same within each group and different from group-to-group. Classification of fuel components in terms of the paraffins-olefins-aromatics groups apparently did not meet the latter requirement. This was verified in tests with single

component hydrocarbon fuels that showed the potential for exhaust reactivity varies widely within each of the fuel component groups of paraffins, olefins, and aromatics. For appropriate classification of fuel components considerably more information is needed on the fuel-derived products of combustion from automotive engines. Given such information, prediction of exhaust reactivity can be made (1) by using either a correlation derived from experimental data, or (2) by the application of product-yield reactivity values to the fuel constituents--individually and/or suitably grouped. The latter approach (2) was tested using experimental data generated in the study. Using some gross assumptions, fuel components were assigned reactivity ratings and exhaust reactivity predictions were made based on these fuel component reactivities and mole fractions. Such predicted exhaust reactivity values were found to correlate well with those for observed reactivity.

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APPENDIX.--ANALYSIS OF EXHAUST MASS EMISSION DATA

The mass emission data for cars 5, 6, 7, 9, and 10 with fuels 12-21 were subjected to an analysis of variance to determine the importance of car effects, fuel effects, and car/fuel interactions on mass emission of hydrocarbon (HC), carbon monoxide (CO), nitric oxide (NO), formaldehyde (HCHO), and total aldehydes (TALD), and the effect upon total reactivity according to the Jackson scale (TRJ). A large car effect, significant at the 99.5-pct level, was found for each of the mass emission parameters. A much smaller fuel effect was observed although the effect was still significant at the 99.5-pct level for all parameters except CO which showed the fuel effect at the 90-pct confidence level. Car-fuel interactions were considered to be negligible as no effect was observed at a confidence level of 90 pct for any of the mass emission parameters. The car and fuel effects are depicted in figure A-1, where the bar for each car represents an average over the 10 fuels and the value for each fuel is an average over the five cars. It is clear that the car differences are indeed larger than the fuel differences for each of the mass emission parameters.

To further explore the fuel effects, the data for each fuel averaged over the five cars, summarized in table A-1, were correlated with 13 fuel physical and chemical properties listed in table A-2. It should be noted that these 13 fuel parameters are not all independent of each other. For example, specific gravity correlates well with 50-pct point and aromatic content. Thus, a correlation between mass emission data and a fuel physical property may be the result of a relationship between the mass emission data and some chemical property of the fuel which also relates to the physical property. With this in mind, our attention is turned to the correlation analysis results which are summarized in table A-3. The HC mass emissions showed a high negative correlation with fuel 90-pct point and mole-percent olefin and a fair positive correlation with fuel isoparaffin content and 10-pct point. Although the CO emissions did not correlate well with any of the fuel parameters, fair positive correlations were obtained with cycloparaffin content and paraffin content and fair negative correlations were observed with olefin content and 90-pct point. The NO emissions showed good positive correlations with specific gravity, 50-pct point, aromatic content, and 90-pct point. Good negative correlations were observed for NO emissions with paraffin and isoparaffin contents. Formaldehyde and total aldehyde emissions correlated well with isoparaffin content and specific gravity. Formaldehyde emissions also correlated fairly well with aromatic content and total aldehydes did fairly well with cycloparaffin content. Total reactivity by the Jackson scale (TRJ) did not correlate well with any of the fuel parameters.

Regression models were chosen on the basis of the correlations discussed above. For those cases where fuel parameters correlated well with each other, only one of the parameters was included in the model. Also, in some of the models OLEF was replaced by PAR + AROM, and PAR was replaced by OLEF + AROM in order to give positive correlations since by definition OLEF + PAR + AROM = 100. Fuel parameters were deleted from the model when their coefficients were not significantly different from zero at the 95-pct confidence level. Results of the regression analysis are summarized in table A-4. Statistically

significant models containing two independent variables (fuel parameters) were obtained for CO and total aldehyde mass emissions. The models for the other four mass emission parameters reduced to the simple linear cases when all insignificant parameters were deleted. The final model for CO containing two fuel parameters (cycloparaffins and olefins, model CO-I) resulted in a correlation much improved over the best of the simple correlations (model CO-II, table A-4) as can be seen by the squares of the correlation coefficients (0.798 versus 0.392). A much smaller improvement resulted from the two parameter models for total aldehydes (0.915 versus 0.824). The best of the simple correlations (one parameter model) for each of the six exhaust mass emission parameters are illustrated in the graphs in figure A-2.

TABLE A-1. - Summary of mass emission data for five cars and 10 fuels

Fuel	Mass emission parameter[1]					
	HC[2]	CO	NO	HCHO	TALD	TRJ
12	25.6	353	43.0	0.677	1.186	13.5
13	26.6	362	41.2	.656	1.126	12.9
14	26.7	355	40.8	.708	1.123	15.1
15	27.3	357	46.2	.597	1.072	12.3
16	28.5	358	40.8	.700	1.285	13.4
17	24.2	333	46.8	.685	1.097	13.3
18	27.9	363	44.4	.590	1.107	11.6
19	25.4	374	43.9	.595	.946	12.4
20	24.6	350	42.6	.633	1.124	12.7
21	25.4	350	46.2	.591	1.077	12.3

[1] HC--Hydrocarbon.
CO--Carbon monoxide.
NO--Nitric oxide.
HCHO--Formaldehyde.
TALD--Total aldehydes.
TRJ--Total reactivity Jackson scale.

[2] All values are averages over triplicate tests with each of five cars expressed as grams per test except for TRJ which is expressed as grams of ethylene per test.

TABLE A-2. - List of fuel physical and compositional properties used in correlations

1. Reid vapor pressure (RVP)
2. Specific gravity (sp gr)
3. 10-pct point in ° F (10 pct P)
4. 50-pct point in ° F (50 pct P)
5. 90-pct point in ° F (90 pct P)
6. Mole-pct paraffin (PAR)
7. Mole-pct olefin (OLEF)
8. Mole-pct aromatic (AROM)
9. Mole-pct monoalkylbenzenes (MonoAlkBz)
10. Mole-pct polyalkylbenzenes (PolyAlkBz)
11. Mole-pct n-paraffins (n-Par)
12. Mole-pct isoparaffins (iso-Par)
13. Mole-pct cycloparaffins (cyclo-Par)

TABLE A-3. - Correlation coefficients for exhaust mass emission levels and fuel physical and compositional properties[1]

	HC	CO	NO	HCHO	TALD	TRJ
RVP	-0.557	-0.291	-0.044	-0.051	-0.016	-0.077
Sp gr	-.241	-.033	.856	-.703	-.746	-.483
10 pct P	.500	.231	.300	-.180	-.108	-.142
50 pct P	-.238	-.387	.797	-.433	-.484	-.208
90 pct P	-.823	-.629	.607	-.002	-.471	.156
PAR	.373	.509	-.856	.437	.423	.348
OLEF	-.856	-.626	.313	.290	-.316	.358
AROM	.161	-.142	.711	-.654	-.242	-.603
MonoAlkBz	.281	.228	.199	-.467	-.099	-.647
PolyAlkBz	.013	-.240	.437	-.213	-.240	.116
n-Par	-.484	-.301	-.274	-.393	-.203	-.332
iso-Par	.612	.052	-.782	.708	.908	.495
cyclo-Par	-.258	.568	.098	-.367	-.733	-.189

[1]Abbreviations of parameters are listed in table A-1.

TABLE A-4. - Summary of regression analysis results

Exhaust mass emission parameter (dependent variable)[1]	Model No.	Fuel parameter (independent variable)	Estimate of coefficient	Standard error of estimate of coefficient	t-value for coefficient	Regression constant	Square of multiple correlation coefficient
HC	I	10 pct P	[2]-				
		90 pct P	-0.0521	0.0127	-4.10	40.9	0.678
		iso-Par	-				
	II	(PAR + AROM)	.217	.0456	4.76	6.27	.739
CO	I	cyclo-Par	.745	.199	3.76	362	.798
		OLEF	-1.328	.327	4.06		
		PAR	-				
	II	(PAR + AROM)	1.189	.532	2.23	246	.384
NO	I	(OLEF + AROM)	.213	.046	4.61	34.0	.726
		90 pct P	-				
		iso-Par	-				
HCHO	I	AROM	-				
		iso-Par	.00270	.00095	2.84	.570	.502
TALD	I	iso-Par	.00494	.00089	5.56	1.000	.915
		cyclo-Par	-.00332	.00122	-2.73		
	II	iso-Par	.00621	.00102	6.11	.947	.824
TRJ	I	AROM	-				
		MonoAlkBz	-.0763	.0318	-2.40	14.2	.418
		iso-Par	-				

[1]Abbreviation of parameters are listed in table A-1.
[2]The dash indicates the parameter was dropped from the model because its coefficient was not significantly different from zero at the 95-pct confidence level.

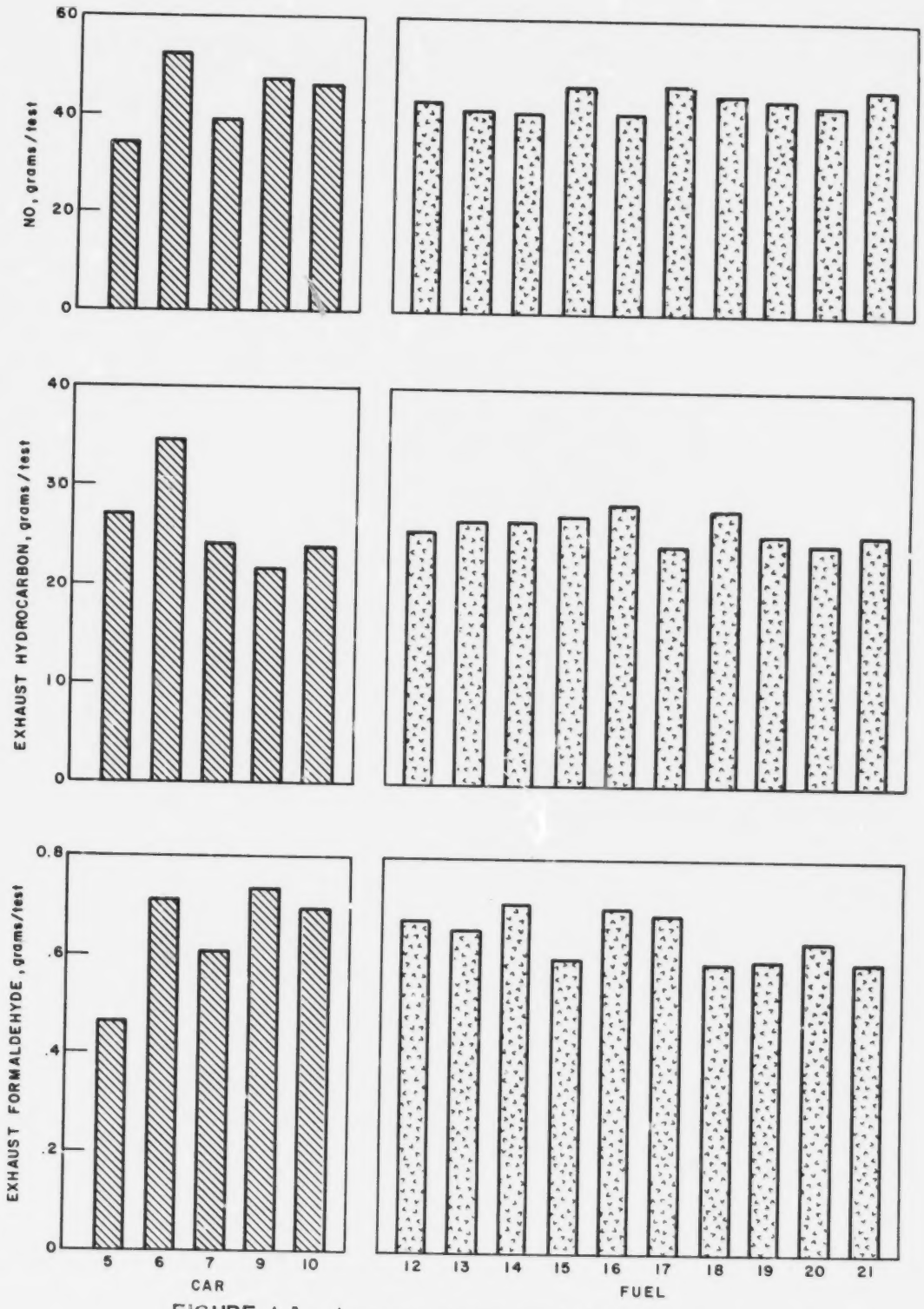

FIGURE A-1. - Average emission levels for each car and each fuel.

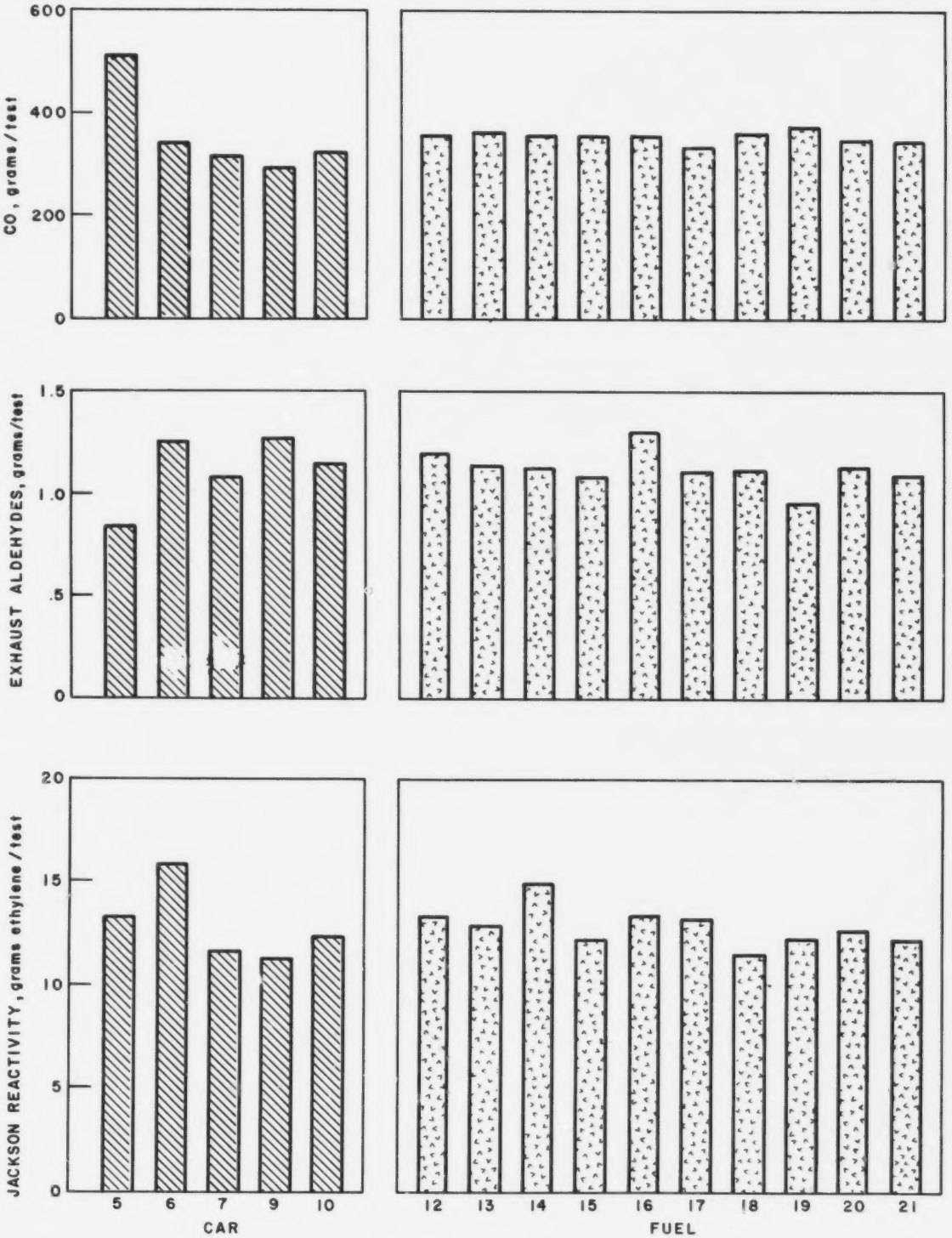

FIGURE A-1. - Average emission levels for each car and each fuel.–Continued

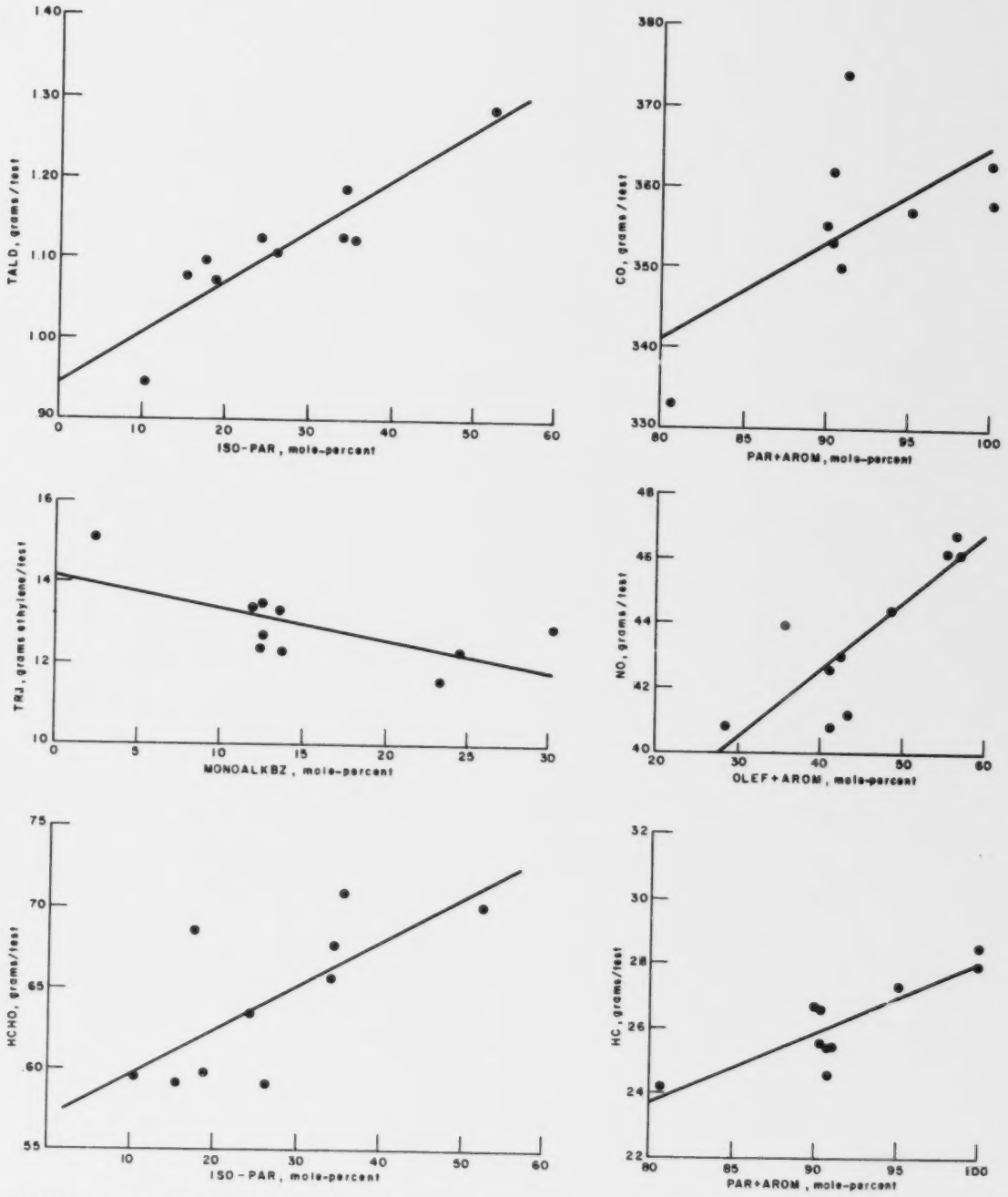

FIGURE A-2. - Variation of exhaust mass emission parameters with various fuel composition parameters.

In brief, correlations between exhaust mass emissions and fuel composition were obtained in all cases. Those for formaldehyde and for total reactivity-Jackson scale may be questionable; the others appear to be fully valid for the sets of fuels and vehicles tested. Although useful as indicators, the correlations obtained in the study may not be reliable in extension to a much broader population of fuels and engines. In this respect it is noteworthy that only relatively small fuel effects were observed despite the great diversity in composition in this set of fuels. For the five cars, the car differences have a far greater impact upon exhaust emission levels than do fuel differences.

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